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Plastics in Engineering

By
John Delmonte
Technical Director
Plastics Industries Technical Institute

THIRD EDITION

MACHINE DESIGN

SERIES

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CLEVELAND, OHIO
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Foreword to Third Edition

Between the second and the third edition a war has come and passed. From that war the plastics industry has emerged greater in stature and more confident of successfully meeting its responsibilities. New materials and new processes underscore the magnitude of the last five years.

Employing the premise of the first and second edition—of analyzing plastics from the viewpoint of the designer and the engineer—the author has extensively regrouped the text material and at the same time introduced a wealth of up-to-date data on the newer plastics. The chapters follow a pattern now of Materials, Properties, Methods, and Applications. The last several years have witnessed the publication of complete engineering information on the properties of plastics, and in consequence, this section, more than any other, has been expanded.

Those data most significant to the practicing engineer and the engineering student have been emphasized.

J. DELMONTE

Glendale, Calif.
May, 1948.

Foreword to First Edition

Rapidity of growth of the plastics industry may be measured by the discovery and development of new synthetic organic materials, improvements and increased facilities in the art of forming and fabricating these materials, and by the progress and extent of their application to engineering problems. It is the latter aspect which this work emphasizes, by discussing numerous applications of plastics to machine design problems and by presenting data conveniently tabulated and classified for reference by the designer. In addition to the survey of engineering features of plastic materials several chapters have been devoted to the chemistry of materials and the art of molding them. It has been the writer's repeated experience that research and development engineers engaged in the design and application of plastics desire to have some knowledge of how these materials are formed and what raw materials are employed in their preparation. In conducting a course on plastics at Armour Institute graduate school during the past few years, the writer has also been able to evaluate the type of information graduate engineers are seeking.

Review of the raw materials employed in plastics, chemical reactions involved in their formulation, and methods of compounding them serve as an introduction to the chemistry of the materials. This information is organized as conveniently as possible for ready reference of engineers. The chemical background is essential to the correct scientific analysis of problems arising in the molding of materials and their behavior in service.

Successful applications of plastics are achieved when the designer understands the potentialities of the materials with which he deals, as well as their limitations. Advantages and disadvantages of plastics are discussed at length in terms of various engineering problems. Numerous tests that the author has conducted are cited to bear out some of these distinctions. In fact, one whole chapter is devoted to the limitations of the more common plastic materials, and the reasons for these shortcomings. Data

on important engineering properties are conveniently tabulated and compared in another chapter. Analyses of some of these properties also are made in terms of the fundamental nature of the materials and correlated phenomena such as condensation and polymerization.

Inasmuch as the large majority of plastics utilized in machine design problems is applied as molded articles, a comprehensive analysis is given of molding problems and mold designs. Laminating, casting, and extruding of organic plastics are discussed in like manner.

While engineering designers do not ordinarily consider surface coatings and synthetic rubbers in terms of plastic materials there are many close relationships. A chapter devoted to each of these subjects bears out those relationships and discusses the engineering properties.

Information contained in some of the chapters has appeared wholly or in part in articles prepared by the author which have appeared in MACHINE DESIGN during the past year or two. The writer wishes to acknowledge the helpful suggestions and encouragement in preparing this manuscript given to him by Laurence E. Jermy. Acknowledgment is also given to Dr. G. Kline for review of Chap. II; Dr. H. Paine for review of Chap. III; Dr. F. Yerzley for review of Chap. XXII; and H. Van Doren for review of Chaps. VIII and IX; also to the following companies for the use of some illustrations and for helpful criticisms by members of their research department on sections of the manuscript: Durez Plastics & Chemicals Inc., Bakelite Corp., Monsanto Chemical Co., Tennessee-Eastman Corp., Plaskon Co. Inc., Reichold Chemical Inc., General Electric Co., Synthane Corp., Formica Insulation Co.

Park Ridge, Ill.
March, 1940.

J. DELMONTE

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Plastics in Engineering

Chapter I
Introduction to Organic Plastics

Development of organic plastics has brought to engineers the world over, new engineering materials which are enriching and broadening the possibilities in both electrical and mechanical design. Their potential utility is unquestioned, and already innumerable applications of these materials have proved their adaptability in the solution of design problems. Though available in forms ranging from soft rubber-like resins to stiff structural members, organic plastics are not offered as a panacea for all problems. The requirements of each application must be studied carefully, and only when the circumstances prevailing are propitious to the proposed materials should approval for their use be given. Misapplication can be damaging, not only to the equipment involved but also to the universal acceptance of plastics. It is only when application is based on the solid background of thorough engineering knowledge that plastics will appear to their best advantage. The fulfillment of this background is not difficult and, unquestionably, engineers will find increasing uses for plastics in the years ahead.

Materials from which organic plastics are derived have been the subject of investigation and experimentation for almost 100 years, though it was not until the early part of this century that the plastics industry became well established. Organic plastics are derivable from a large number of sources which are broadly classified as synthetic resins, cellulose derivatives, natural resins, and protein matter. One of the most prolific sources of plastics is the group of synthetic resins. Research on the phenomena of

synthetic resin formation and the polymerization of resins occupied the attention of numerous research chemists during the latter part of the 19th century, as it does today. However, lack of precise scientific control retarded the commercialization of these materials until Dr. Baekeland published the results of his investigations on phenolic resins in 1909, and paved the way for the rise of the plastics industry.

The success of a plastic material depends not only upon the properties which it displays, but also upon the availability and cost of raw materials used in its manufacture. In the tireless search for synthetic materials, the chemist turns to inexpensive raw materials such as farm by-products, coal, ammonia, cellulosic products, petroleum products, and many others. In addition, chemical treatment and processing of the materials must not be too costly, if the finished products are to be commercially feasible. Chemical literature, replete with new evidence and data on the development of synthetic materials, indicates that newly developed materials number in the thousands. Of these, perhaps a few dozen have attained industrial importance. Notwithstanding, the theoretical background afforded by researches upon synthetic resin formation and the development of cellulosic derivatives have contributed immeasurably to the success and understanding of the present materials.

Activities in new material developments from within the plastics industry and the promulgation of new applications by the consumers of these materials have combined in recent years to give new impetus to the growth of the industry. This accelerating activity commenced during the Second World War, and with the cessation of hostilities brought forth numerous industrial uses for plastics which had not been conceived in pre-war periods. Particularly impressive are the contributions plastics are making to other industries such as those engaged in the production of textiles, rubber, plywood and lumber, ceramics, and metals. In evaluating the engineering aspects of plastics it will be necessary to refer to the numerous combinations of plastics with other materials.

On the pages immediately following are outlined some of the historical backgrounds of the more important plastic materials. In particular, those features and developments which possess engineering significance are discussed. A few statistics also have been selected to emphasize the growth of the industry.

Cellulose Derivatives

The first synthetic plastic material to attain industrial significance is acknowledged to be a cellulose derivative, nitrocellulose or "Celluloid". Much credit for its early development is due John Wesley Hyatt, who in 1868 undertook the development of an ivory substitute for billiard balls. He prepared nitrocellulose by reacting nitric acid upon cotton linters, and then compounded this product into a useful plastic with the aid of camphor. Professor Schonbein had investigated nitrocellulose in Germany quite a few years before Hyatt, and A. Parkes prepared nitrocellulose plastic sheets in England, which were described in 1865 (British Patent 1313). However, industrial manufacture of nitrocellulose plastic materials did not commence until the early 1870's. In the United States, the Albany Dental Mfg. Co., succeeded by the Celluloid Mfg. Co. in Newark, N. J. in 1871, became the first to produce the new material, while in England the British Xylonite Co. was organized for the same purpose.

At first these synthetic materials were marketed as substitutes for ivory, tortoise shell, and mother of pearl. Brush backs, combs, collars, cuffs, and a wide variety of novelties featured the early efforts of the manufacturers of nitrocellulose. Improvements in manufacturing methods and in the quality of the final materials led to wide-scale use of the materials in industrial and decorative applications. Significant was the preparation of the first safety glass in 1906 (U.S. Patent 830,398) by Wood, who cemented clear nitrocellulose sheet between plate glass faces.

The inflammable nature of nitrocellulose and the lack of permanency in the finished products led to the development of other cellulose derivatives both in this country and abroad. Most noteworthy is cellulose acetate, which underwent development in the early 1900's. Many of the initial applications of this material were in thin film form or as sheets, rods and tubes, replacing the more inflammable nitrocellulose. Eichengrun, who first contributed to the development of cellulose acetate plastics (U.S. Patent 738,533 in 1903), later investigated injection molding in 1919, though the idea was suggested in an earlier patent of Hyatt. The first molding powders of cellulose acetate began to make their appearance in 1929 and 1930, and with the development of injection molding machines this production gained in momentum. From 1934 to

1938 cellulose acetate practically replaced all nitrocellulose in the manufacture of automobile safety glass, though in turn it was replaced by a vinyl resin.

Other cellulose derivatives made their first appearance as surface coatings in 1932. Among these was cellulose acetate butyrate which in 1938 was developed as a molding compound to fulfill some of the many demands of injection molding. Ethylcellulose also underwent commercial development and application during this period, first as a coating and later as a molding and extruding compound. Among the more recent members of the cellulosic family are cellulose propionate and cellulose acetate propionate, both introduced commercially as molding materials. Emphasis was placed upon toughness and dimensional stability.

Growth of cellulose plastics in the United States may be traced in the following statistics:

Cellulose Plastics—Total Production (Pounds)

1938	23,712,723	1943	68,428,529
1939	34,169,007	1944	80,976,495
1940	35,765,340	1945	91,770,992
1941	53,433,787	1946	121,231,200
1942	63,374,651	1947	90,000,000 (est.)

These statistics do not include another cellulose derivative, regenerated cellulose (rayon), which from a world production of 6,250,000 pounds in 1930 has grown to an estimated 2,025,000,000 pounds in 1942. United States production of rayon approached 800,000,000 pounds in 1945.

Casein Plastics

Casein plastic materials have an early origin as do many other plastics. At first, unknown to each other, a German printer and a German professor were applying themselves to the problem of hardening casein and making it waterproof. The printer, W. Krische, conceived the idea of coating white cardboard with a casein solution and treating it with formaldehyde, while A. Spitteler endeavored to produce a waterproof casein for a writing tablet. The two collaborated to produce a tough, insoluble horn-like mass from casein (German Patent 127,942 and U. S. Patent 646,844). The first successful casein developments in this country were by Aladdinite Co. in 1919, though the Galalith Co. of Ham-

burg commercialized the process at an earlier date.

Casein plastics have never become important competitors of cellulose plastics, though they have established their own markets as colorful decorative materials, low in cost, and capable of taking a beautiful polish. World production of casein plastics was estimated at 9000 to 10,000 tons before the Second World War, though this figure undoubtedly has increased considerably since 1943 when commercial production of casein fibers for textile manufacture was undertaken. Casein has long been the base of one of our most versatile adhesives, and considerable quantities are used each year by the woodworking industry. Engineering applications of molded casein plastics have been comparatively limited due to the difficulty of molding the material and its susceptibility to water absorption.

Other chemically related materials, the soyabean protein and zein (corn protein) may be noted. Large quantities of soyabean protein are employed as adhesives for the manufacture of Douglas fir plywood. Zein, on the other hand, has found its greatest outlet since 1942 as a waterproof coating for wrapping papers.

Shellac Plastics

While engineering applications of shellac plastics have decreased in recent years due to the appearance of superior synthetic resins, they warrant some examination because before the advent of synthetic resins there were many noteworthy applications of shellac plastics to mechanical and electrical products. Shellac enjoyed extensive use as a molding composition and, while early patents in 1868 of Merrick (U. S. Patent 85,018) and Gardner (U. S. Patent 73,088) discuss the molding of shellac, its production did not attain appreciable proportions until the development of phonograph records in 1895. Shellac has also been extensively employed as a resinous binder for cloth, paper, and mica insulation. Its resistance to electrical arcing has also made it desirable in many electrical applications.

Bitumen-Base Plastics

Bitumen or asphaltic-base compositions have always played an important part in the manufacture of molded industrial articles. Introduced to this country by E. Hemming in 1909, bitumen

plastics have been called cold-molded plastics because they are shaped at relatively low temperatures. The materials are either pre-warmed and formed in a cold mold, or else they may be formed at room temperature and then baked to achieve their strength.

Without benefit of much fanfare or publicity the bitumen or asphaltic-base plastic has fulfilled many applications in the electrical and automotive field, as for example in the manufacture of switch parts and storage battery cases. Many of its earlier applications have now been replaced by molded synthetic resins.

Phenolic Plastics

The plastics industry in the United States dates back to Dr. Baekeland's discoveries of the condensations of phenols with formaldehyde to form a resin. Though the phenomenon was observed by several investigators starting with Baeyer in 1871, no industrial significance was attached to the resinous mass that was formed. It remained for Dr. Baekeland to discover the fundamental reactions, establish a correct scientific control and, at the same time, demonstrate the efficacy of heat and pressure in molding the materials. For a few years prior to 1909 Dr. Baekeland worked on these materials in his Yonkers laboratory, finally announcing his findings in 1909 and filing patent claims. Included in his early patents were molding compositions of wood-flour and asbestos-filled phenolics, and laminated "Bakelite-Micarta". Prior to the publication of his results and demonstrations of what could be done with these synthetic resins, no industry in this country or abroad had manufactured infusible, insoluble, solid plastics of engineering utility. Other early pioneers in this work were Raschig of Germany and Redman and Aylesworth in the United States.

Industry was quick to recognize the potentiality of the new synthetic material which possessed high strength, moldability, and durability. It soon found many applications as insulation in the electrical industry. The automotive industry was among the early sponsors of this material, and a corporation was formed in 1917 to devote its facilities solely to the production of phenolic plastic automotive goods. Among early items was a steering wheel, which consisted of a wooden core about which was molded a ¼-inch thickness of molded phenolic plastic. Addition of heating wires to this assembly overcame some of the discomforts of cold-weather

driving. Other early molded parts on automobiles included ignition parts, radiator caps, knobs and handles.

At this early date, the possibilities of phenolic plastics as strong, durable insulating materials were recognized by Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa., which undertook the development of "Micarta". This laminated material was applied to a number of gears and pinions. Various types of gears appeared, some with shroud rings, others without. The advantages of resilient, quiet gears of laminated phenolics became apparent at this time, and other companies followed suit in fabricating gears from these materials. An important decision was reached in 1921 when the courts voided the early Conrad patents (U. S.-1,167,742 and 1,167,743) covering the use of laminated phenolics in gear construction, permitting the entire industry to fabricate gears from plastics. In this same period the application of laminated phenolics to airplane propellers evoked considerable attention.

In the meantime Dr. Baekeland was successful in upholding his many broad patents on the preparation and development of phenolic plastics. Matters were brought to a head in 1922, when the Bakelite Co. sued the customers of their closest competitor, Redmanol Co., for employing molding materials covered by the Baekeland patents. The Redmanol Co. lost out in the courts and, as it was impractical for that company and its subsidiary (the Condensite Co.) to continue, the three organizations merged to form the Bakelite Corp., New York, naming Dr. Baekeland as its first director. Progress now ensued at a rapid pace and 1926 and 1927 found extensive applications of molded phenolics, notably as electrical insulation and in the automotive field.

By 1926 and 1927 the original Baekeland patents had begun to expire. and new companies began to prepare and market phenolic plastics. The infusion of new blood and new ideas gave the industry a decided impetus and the volume of trade began to grow by leaps and bounds to its present high volume. Phenolic plastics began to branch out in many directions. The surface coating industry was quick to recognize the advantages of the hard, durable coatings prepared from a special form of oil-soluble phenolic resins; interest in adhesives emanated from the commercial development of phenolic resin films for plywood (Tego film) in 1935; developments in resin-bonded grinding wheels and

brake bands were widely accepted; and extensive applications were developed for laminating compounds and laminated parts. The appearance of formed laminated phenolic parts in 1943 focused attention upon the possibilities of using plastics to replace sheet metal in the design of machines.

The appearance of cast phenolic plastics in 1932 opened new fields of application in which color and decorative effects were emphasized. Ranging from water-white transparency to various degrees of translucency, the cast phenolics attracted much attention. These materials also lent themselves to easy machining and finishing operations. During the Second World War, cast phenolics weighing up to a ton proved successful in the manufacture of large forming blocks. These forming blocks, or dies, could be manufactured in a few days and assisted in the fabrication of aircraft components.

The recent molding activity in phenolics indicates a 50 per cent increase over the volume of phenolics molding in 1941, which in turn is about four times as large as the activity in 1930. Complete statistics on synthetic resin production up to 1938 appear in a report prepared by the U. S. Tariff Commission (Report 131, 1938). Tradenames for phenolic plastics in all of these fields are quite extensive, probably numbering well over 100. Some of the better known types, however, are: Molding Compounds—"Durez", "Bakelite", "Durite", "Makalot", "Textolite", "Resinox", etc.; Laminated Plastics—"Formica", "Spauldite", "Synthane", "Micarta", "Panelyte", "Dilecto", "Lamicoid", etc.; Casting resins —"Catalin", "Marblette", "Durez", etc.

Urea Formaldehyde

For a number of years, up to 1930, requirements of organic plastics consumers were satisfied by the infusible phenolic plastics, the cellulose plastics, and casein plastics. Phenol plastics were unrivalled in the fact that they were the only commercially feasible, moldable, infusible solid plastic. A need was felt, however, for a moldable, infusible plastic with a wide variety of color selection. The urea plastics gave evidence of fulfilling this need. H. D. Bennett, president of Toledo Scales Co., Toledo, O., in recognizing the sales possibilities of an improved, moldable, multicolored translucent plastic as housing for his weighing machines, person-

ally sponsored several fellowships on plastic research at the Mellon Institute of Industrial Research, Pittsburgh. After exhausting the possibilities of other materials, a concerted effort was made to develop a practical urea-formaldehyde plastic.

The condensation of urea with formaldehyde was not a new discovery. As early as 1897, a German had discovered an amorphous, resinous condensation product resulting from the reaction of urea with formaldehyde. At this time, the world was not plastic conscious, and the advantages of synthetic organic materials was unknown. Until about 1925 developments in urea formaldehyde molding compositions had not made much progress. Early patents by Dr. John (U. S.-1,355,834) and Dr. Pollack (U. S.-1,458,-543) marked the early efforts. Another significant development, which took place in the late twenties, undoubtedly fired the imagination of those engaged in urea-formaldehyde research. Low cost urea was made available by a new process of the I. G. Farbenindustrie A. G., Germany, which synthesized urea from nitrogen.

An American firm in 1929 bought the foreign rights to a process for manufacturing urea plastics, and in 1930, 200,000 pounds of moldable thio-urea plastics were produced. The thio-urea plastic differed slightly from urea plastic in that it contained sulphur. The new plastic was called "Beetle," and its products in the field of household articles called "Beetleware."

In the meantime, progress had been made at the Mellon Institute of Industrial Research, Pittsburgh. After thorough systematic research, a satisfactory moldable urea formaldehyde plastic was developed. Resinous products were produced only after intensive research revealed the optimum combinations and procedures to follow. The result was a practicable, moldable urea plastic which formed an infusible, synthetic material. The machine housings of the Toledo Scales Co., Toledo, O., now molded of urea plastics, were reduced considerably in weight and improved greatly in appearance, establishing new sales records. The Plaskon Co., Inc., Toledo, O., emerged to enter the production of urea formaldehyde in 1931 as a competitor to "Beetleware." A third organization entered the market in 1932, when Carleton Ellis took out new patents for the manufacture of a moldable urea plastic. This third organization, the Unyte Corp., merged with Plaskon in 1936. to form the Plaskon Co. Since that time other plastic

material manufacturers have entered the production of urea plastics. In 1940, the Plaskon Co. was taken over by the Libbey-Owens-Ford Co.

During the Second World War, the number of urea resin moldings appears to have decreased though this was compensated for by an increasing activity in the adhesives field where the greatest volume is consumed.

More recent trends in utilization of urea resins are indicated by its applications in the textile industry to improve the quality of natural fibers, and its introduction into paper manufacture, where the presence of only a few per cent of resin greatly improves the wet strength of paper.

Melamine formaldehyde resins chemically resemble the ureas and are of more recent origin. Because of their better water and temperature resistance, they have replaced a number of molded urea parts, or at least are employed in combination with the ureas. Melamine-formaldehyde plastics, introduced in this country in the early 1940's, are produced by American Cyanamid Corp. and Monsanto Chemical Company. The melamines have exhibited better temperature and moisture resistance than the ureas. Both melamine and urea resins fulfill important roles as laminating agents, adhesives, and as hard, baked enamel coatings.

Vinyl Resins

Vinyl resins have been the subject of intensive commercial development during the past fifteen years, though the chemistry of vinyl resins has been studied at length for a much longer period of time. As early as 1838 it was observed that when sealed tubes of vinyl chloride were exposed to sunlight a white precipitate formed. However, the intervening years contributed little to the commercial development of these materials. Staudinger's fundamental studies in Germany on the mechanism of vinyl polymerization, paved the way for the industrial awakening of these materials. In this country early efforts of the Shawinigan Chemicals Corp. and Carbide and Carbon Chemicals Corp. in the late 1920's resulted in the general availability of vinyl resins. Copolymers of vinyl chloride and vinyl acetate were introduced during the early 1930's as coatings, sheets, and molding compounds. Rigid and nonrigid sheets emphasized the versatility of these materials.

Early noteworthy patents on the vinyl esters were granted to Lawson (U. S. Patent 1,867,014—1932) and Ostromislensky (U. S. Patent 1,721,034—1929).

Another group of vinyl resins, the vinyl acetal series, was developed during the same period (U. S. Patent 1,746,665—1929) by reacting aldehydes upon polyvinyl alcohol. These materials attained much prominence when in 1938, as polyvinyl butyral, they replaced cellulose acetate as the plastic interlayer in automobile safety glass. Further applications during the past few years have been in the field of waterproof coatings. Important electrical insulation was fulfilled by another member of this series, while their toughness was reflected in applications such as nonmetallic hammer heads.

Polyvinyl chloride resins and their copolymers are achieving considerable prominence as coating materials for both textiles and papers, and as extruded tubing and conduit. In fact, they are beginning to surpass the phenolics in production volume. B. F. Goodrich Chemical Company and Dow Chemical Company have recently pioneered developments in polyvinyl chloride resins.

In general, exceptional chemical resistance is offered by certain lacquers of the vinyl resin series in proprietary coatings such as "Tygon" and "Amercoat". "Vinyseal" adhesives also have gained acceptance as general utility materials. The production of vinyl compounds has risen tremendously since 1940 and today is on the same level of volume production as alkyds and phenolics (about 130 million pounds annually).

Acrylic Resins

A branch of synthetic resins, somewhat similar in molecular structure to the vinyl resins, are the acrylic resins. As with so many other synthetic materials, their industrial importance was attained many years after the accidental discovery of their preparation. A solid substance obtained from the oxidation of acrylic acid by Redtenbacher (1843) was the subject of investigation by another chemist in 1872, who found that the material swelled in water. Sunlight converted these substances into a clear, hard, transparent mass. The seeds of the industrial development of acrylic resins were sown when Rohm published his thesis results in 1901, describing methyl-acrylate polymers and polyacrylates of

high molecular weight. About ten years later, Rohm resumed work on polyacrylates, taking out patents for their use as rubber substitutes and in drying oils. In 1927 the Bauer synthesis was used as the starting point for the production of a small quantity of methyl-acrylate in Germany. By 1931, the Rohm & Haas Co. began production of limited quantities in the United States. Transparent sheets and tubes of remarkable clarity were produced, and used on aircraft. Polymethyl methacrylate was proved to be the substance best suited for industrial purposes. Finally, the preparation of moldable methyl methacrylate was developed in turn by the E. I. du Pont de Nemours & Co., Arlington, N. J. and Rohm & Haas, Philadelphia. Molded products of this material began appearing in 1937. As transparent windows, they have been widely applied as covers for industrial apparatus subject to frequent inspection. Much of the recent production of acrylic resins has appeared in aircraft.

The curved shapes of all of the bomber noses and blisters, and canopies of fighter aircraft have necessitated considerable effort in developing fabricating techniques for handling the large transparent sheets without distorting them. A new innovation, introduced on the B-29 bomber in 1944 was the appearance of a laminate of two acrylic sheets with a core of polyvinyl butyral, for added toughness and durability. Improved temperature-resisting grades for molding have appeared in recent years.

Polystyrene Resins

Polystyrene resins have attracted industrial interest within the last few years. Several large chemical companies are engaged in its production in the United States. It is one of the oldest synthetic resins, having been produced as early as 1839. Dr. F. Matthews of England is accredited with an intensive research on the polystyrene resins, the results of which were published in 1911. His practical suggestions have been valuable guides in the work that followed. The Dow Chemical Co., Midland, Mich., began the manufacture of styrene late in 1937. Bakelite Corp. and Monsanto Chemical Co. are both pioneers in the preparation of compositions of polystyrene.

Polystyrene has always been recognized as a splendid insulating medium for high-frequency radio equipment and other elec-

trical apparatus where dielectric losses are of primary concern. When first introduced into the United States in 1933, it was marketed in the form of a varnish for radio equipment. Recent developments in this country and abroad have made the material available as molding powder, fine threads, and thin films. Exhibiting excellent physical and electrical properties, polystyrene has become the most widely used injection molding material.

During the Second World War the production of styrene grew more rapidly than any other material, attaining a rate of 40,000,000 pounds monthly in 1945. The great bulk of this, however, went into the manufacture of synthetic rubber of the butadiene-styrene copolymer type. Recent developments in injection molding of polystyrene parisons and blow molding of hollow shapes such as bottles, presage a large potential outlet for the materials. The appearance of polydichlorostyrene in 1944 through the efforts of Mathieson Alkali Works Co. and Dow Chemical Co., made available a new promising material with better heat resistance than polystyrene.

Alkyd Resins

While of greater importance to the surface coating industry, the development of alkyd resins is of fundamental importance to the plastics industry. Initial work on the reaction products of glycerol and phthalic anhydride (alkyds) began in the 1910's when the cost of producing phthalic anhydride reached a low level. Developments were accelerated in the early 1930's when drying oils were combined with the alkyd resins, and much fundamental study was devoted to the subject by Kienle (U. S. Patent 1,893,872-3—1932). Maleic anhydride also began to make its appearance as an important component of alkyd resins in this period. The total production of alkyds reached 47,000,000 pounds in 1936, 61,000,000 pounds in 1937, 178,000,000 pounds in 1943, and 188,000,000 pounds in 1945. "Beckacite" and "Beckosol" resins by Reichold Chemicals Co. and "Glyptal" resins by General Electric Co. are examples of the coating grades and insulating grades of alkyd resins.

Alkyd resins are less important to molding materials than surface coatings. However, they have been used as binders for mica-splints and flakes to produce useful insulating materials.

There are other uses in gaskets, laminated fabrics, and papers. Desirable properties are obtained through modification with drying and non-drying oils, fatty acids, and natural or synthetic resins.

During 1943 and the years following, a number of new resins were introduced which resemble the alkyds in that they are esters, products of reaction between alcohols and acids, but which undoubtedly will form a group all of their own known as the polyester resins. These resins form the basis of the low-pressure laminating techniques which have proved so popular in developing structures combining high strength with low weight.

Polyamides—Silicones—Polyethylene

Brief historical notes will be made on three more plastic materials which show a great deal of promise in engineering applications. These are the polyamides (nylon), silicones, and polyethylenes. All of them attained industrial importance from 1943 to 1947.

POLYAMIDES: In 1935 Dr. W. H. Carothers of the duPont company first synthesized a superpolymer showing much promise as a textile product. Efforts were directed toward producing the chemicals required for the manufacture of these materials, and first commercial applications of the polyamides began to make their appearance in the 1940's. Carother's early patents are considered basic (U. S. Patents 2,071,250 and 2,071,253—1938). Woven textile products and monofilaments determined the first applications of these plastics, though more recently, high-temperature resisting moldings have made their appearance. Another form of polyamide resin for coatings and adhesives was introduced by the General Mills Corp. in 1945.

SILICONES: Bridging the gap between ceramics and plastics the silicone resins are some of the most promising materials yet to be developed. Due to the efforts of the Corning Glass Works and the Dow Chemical Co. (Dow-Corning Co.), silicone resins were made available as liquids and greases possessing unusual viscosity stability over a wide range of temperatures (U. S. Patent 2,371,-050—1945 and British Patent 561,136—1944). In the meantime the General Electric Co. undertook the development of silicone resins as a high-temperature resistant insulating compound (see

U. S. Patent 2,258,218 to 22—1941). The silicones, in conjunction with glass fiber reinforcement, have greatly extended the scope of electrical insulating materials, increasing the capacities and operating temperatures of electrical equipment. Surface coatings and high-temperature-resistant rubbers are among the useful forms assumed by these versatile plastics in recent years.

POLYETHYLENES: Largely a British development, the polyethylene resins are a notable contribution to the nonrigid types of plastic materials. Involving high-temperature, high-pressure reactions, a group of notable plastics has been produced (U. S. Patent 2,153,553—1939). In this country the materials were first made available in 1943 as molding compounds, sheets, and foils by the Carbide and Carbon Chemicals Corp. and the E. I. du Pont de Nemours & Co. Their inherent flexibility and good dielectric properties make them valuable materials for use in electrical equipment. A related material, polytetrafluoroethylene, developed in 1946, has outstanding chemical and temperature resistance.

Total Production of All Synthetic Resins in the United States (Pounds)

1936	141,945,676	1941	437,799,000
1937	162,104,713	1942	426,731,000
1938	130,358,000	1943	651,511,000
1939	213,027,548	1944	780,000,000
1940	276,814,000	1945	808,000,000

Organization of the Plastics Industry

In its broadest implication the plastics industry embraces those organizations engaged in research and development of materials from which resins and plastics are derived, to the industrial consumer engaged in the design and application of the finished product.

Primary Material Manufacturers: Heading the organization chart for the plastics industry would be the primary material manufacturers who are engaged in the production of cellulose derivatives, synthetic resins, and the development of materials from natural origins such as farm products, protein substances, lignin matter, insect, and tree excrements. Production of these materials may constitute highly specialized operations and, in consequence, primary material manufacturers may be grouped in accordance with the nature of the compositions which they prepare. Several relationships may exist; for example, some material manufacturers

prepare only cellulose acetate, nitrate, and ethylcellulose, furnishing these to other material manufacturers who compound them into molding compositions. On the other hand, a molding material compounder may nitrate or acetylate his own cotton, as well as prepare the compositions. Further, the relationships grow less well defined when large custom molders feel that their volume of business warrants the production of resins of their own manufacture. There are even cases where industrial consumers have felt that economies are derived not only in molding their own products, but also in producing their own resins. However, overlooking these special relationships for the sake of clarity, *Fig.* 1 outlines the organization of the plastics industry.

Converters of Plastic Materials: Engineers and designers come into contact more frequently with converters of plastic materials than with the primary material manufacturers, inasmuch as the former engage in the fabrication or compounding of materials to customer specifications. A greater proportion of molding operations is conducted by custom molders in accordance with the designs submitted by industrial consumers. Molds are purchased by the consumer and are regarded as his property and equipment. Other operations sometimes are employed by the custom molder such as buffing of flash lines, drilling of holes, wiping-in enamel, or roll-leaf stamping on the molded part. Inserts to be molded into position usually are furnished by the recipient of the molded articles.

Laminated material manufacturers may or may not fabricate their laminated products. Often the industrial consumer prefers to fabricate his own parts from laminated sheets or tubes. Fabrication may entail punching of pieces from sheet stock, turning down small pieces on automatic screw machines, or machining small gear blanks. Though much of this fabrication is conducted by the consumer, there has been a tendency for laminated materials manufacturers to specialize for specific industrial requirements. Thus one manufacturer may devote his facilities to nonmetallic gears or bearings, while others may turn to insulation for radio equipment, architectural materials, aircraft pulleys, etc. The specialized requirements usually entail more than laminating between flat polished platens, in that the process may be more correctly described as a hot-forming procedure, thus bridging the gap between molding and laminating. Engineers turn to laminated

PRIMARY MATERIAL MANUFACTURERS

(Manufacturers of Synthetic Resins, Cellulose Derivatives, etc.)

Molding Compositions

Resins for Laminating

Resins for Casting

Resins for Surface Coating

Miscellaneous Uses in Bonding, Adhesives

SECONDARY MATERIAL MANUFACTURERS

(Custom Molders, Laminators, Compounders of Surface Coatings, etc.)

Molded Products

Laminated Sheets, Rods, Tubes, Bars

Cast Bars, Sheets, Rods, and Special Castings

Lacquers, Varnishes, Enamels

Plywood, Grinding Wheels, Resistors, Textiles, etc.

INDUSTRIAL CONSUMERS

(Design Engineers and Industrial Consumers for Products and Machines)

Applications in: Electrical, Mechanical, Chemical, and Decorative Arts Fields

Fig. 1—Organization chart for the plastics industry

phenolics when large, high-strength sections of plastic materials are required.

More recent activities in the field of low-pressure laminating make possible the development of large curved shapes for aircraft structures, building structures, and boats. These activities are an important division of the plastics industry and obviate the need for costly molds which always are required in conventional molding. The casting of large plastic forms and tools to specifications is another growing branch of the plastics industry, as well as the extrusion industry which is engaged in the manufacture of rods, tubes, and shaped bars of miscellaneous cross sections. Comparison of the number of companies engaged in converting plastic materials in 1941, 1944 and 1947 shows the growth of this branch of the plastics industry:

Number of Plastics Converting Companies*

Activity	1941	1944	1947
Compression Molding	400	800	890
Injection Molding	200	320	550
Extrusion Molding	...	112	...

* Some companies may be engaged in more than one of the above activities.

If one were asked which quality of plastic materials it is that makes them such interesting materials to work with, he undoubtedly would reply "versatility." There are plastics hard enough to abrade tool steels and others fluid enough to use as lubricants, although generally they are classified as rigid and nonrigid varieties. Some plastics possess tensile strength and elongation comparable to the best rubbers; others are as transparent as glass. Plastics are truly chemical materials capable of adjustment to meet the many demands of engineering specifications.

Plastics in Machine Design: The excellent utility of plastics as engineering materials is substantiated by numerous mechanical applications. Their low moduli of elasticity, as compared to the more common metals, will work to advantage in some designs and at a disadvantage in others. For example, the inherent resiliency of plastics make them suitable for quiet running gears or for the construction of panels where much mechanical scuffing is present. A low modulus means that an automobile fender of sheet plastic is less apt to suffer permanent damage than a sheet metal fender. Then too, plastics lend themselves to the construction of

composite laminates having low-density cores and strength-weight ratios comparable to the best metals. Nevertheless, thickness for thickness, sheet metal is much stiffer than plastics and more suited to structural applications.

The low density of plastics, averaging about 0.05 pounds per cubic inch, has influenced the design of portable machines and a wide variety of miscellaneous articles. The density may be varied from 3 pounds per cubic foot for light-weight foams to 350 pounds per cubic foot for metal-powder filled plastic bullets. Plastics will resist a wide variety of chemicals which attack the more common metals, yet most plastics have difficulty in withstanding boiling water. The designer of machines should understand plastics and know their limitations before applying them.

Ease of moldability and the precise reproduction of design details, without the necessity of subsequent finishing operations, are the outstanding qualities which appeal to machine designers. Molded plastics appear to their best advantage when they are used in the duplicate manufacture of many thousands of parts with the utmost fidelity.

Plastics in Electrical Insulation: As solid insulating materials of relatively high strength, organic plastics are invaluable. When these materials first made their appearance, the electrical industry commenced utilizing them to fulfill insulation requirements of all descriptions. Radio and electronic equipments have provided important outlets for many types of laminated and molded plastics. Outstanding performance at ultra-high frequencies has been exhibited by such plastics as polystyrene, polydichlorostyrene, and polyethylene, while at lower and power frequencies the phenol formaldehyde and melamine formaldehyde materials function as general purpose insulation. From thin protective insulations on magnet wires to heavy, solid dielectrics in high-voltage transformers, plastics have given reliable performance.

Plastics in Chemical Equipment: Organic plastics are assuming increasing importance in the field of chemical processing industries. Naturally resistant to corrosive gases, liquids, and chemicals, they are influencing the design of chemical apparatus or equipment subject to corrosive conditions. Hard rubber, stainless steel, Monel metal, and nickel-clad apparatus have been employed extensively in chemical equipment, though plastics are making a serious bid for recognition. Hot-acid handling apparatus

and pipe lines, and numerous applications in the electroplating room are but a few of the many typical uses. If not in molded or laminated form, the plastics may serve as protective coatings for aluminum or steel, or as binders for ceramic bricks. Chlorinated polymers, such as chlorinated rubber and polyvinylidene chloride, and fully-saturated polymers such as polyethylene, polytetrafluoro-ethylene, and polyisobutylene, have shown exceptional resistance to the strongest acids and alkalies.

Plastics in Optical Equipment: A large number of the plastics are available in transparent forms, which are easily machinable or readily moldable. One-half the weight of glass and much more resistant to breakage than inorganic glass, the transparent plastics as engineering materials are in a class by themselves. The more optically clear varieties and the more weather-resistant types have found their way into all types of aircraft. Aside from these important uses, transparent machine models to aid the designer, models for photoelastic analysis, manufacture of safety glass, rapid reproduction of lenses for low cost optical goods, and many other applications indicate their versatility.

Plastics as Heat Insulators: The resistance of solid organic plastics to high temperatures is relatively poor as compared to most metals, with few exceptions. Formulated to be molded or laminated with heat, plastics still retain a degree of heat susceptibility, as manifested by variations of physical and electrical properties with changes in temperature. However, as insulators for the home or for low-temperature apparatus, the low-density foams prepared from plastics, with their low K-factors, present properties favorable for such use.

Recognizing that the temperature limit of most plastics is under 300 F, designers nevertheless utilize their heat insulating properties and low thermal conductivity by specifying plastics for control knobs and buttons, where it is desired to reduce heat flow to the hand. In the simplest example, it is better to make the frying pan out of metal, and the handle for the frying pan out of plastics. With the exception of tetrafluoroethylene and silicones, no plastic is safe above 500 F.

Plastics and Woods: Both as adhesives for wood veneer and as impregnants for wood, plastics have teamed with woods to offer superior materials. From the role of reducing splits and checks in seasoned lumber to high-density laminated airplane propeller hubs

and blades, plastics find entry in the wood industry. Plywood faced with thin films of resin treated papers or textiles has become not only much more decorative, but also much more weather resistant. Hot-setting synthetic resin adhesives have made possible efficient construction of laminated boat keels and large droppable aircraft fuel tanks.

Plastics and Paper: Resin-impregnated papers have long been standard in the manufacture of certain grades of laminated plastics. More recently the introduction of a small percentage of urea or melamine resin into the beater of the paper forming machine, resulted in the development of a high wet-strength paper. On the other hand, plastics may be applied to papers as protective coatings, giving them grease and oil resistance, or greater gloss; they may function as sizing agents, or at least make their appearance in the manufacture of printing inks. Beyond these applications there are developments such as the resin-pulp preforms which are employed in molding thin diaphragms to large automobile body components.

Plastics and Rubbers: It is becoming increasingly difficult to draw a distinction between rubbers and plastics, because many plastics are rubber-like when judged by their elongation, and many natural rubber derivatives have been treated to be used as moldable plastics. Styrene and acrylo-nitrile, important synthetic resins, are both employed extensively in the manufacture of synthetic rubber. Most rubber manufacturers offer some of their industrial rubber mechanical goods in formulations based upon synthetic resin elastomers which possess outstanding oil, gasoline, or grease resistance. Composite laminates of vulcanized rubber stocks and faces of organic plastics are useful as vibration absorbers.

Plastics and Textiles: There are many evidences of the close co-operation between the textile manufacturer and the plastics material producer. Numerous plastics are now being widely used by the textile manufacturer for dress goods and industrial fabrics. The need for synthetic resins became apparent when our armed forces invaded the South Pacific islands, where bacterial growths rapidly decomposed cotton and woolen goods. From parachute harnesses to brushes for sewage disposal plants, textiles prepared from plastics are very much in evidence. If not comprising the base fiber, plastics are employed as impregnants for natural fibers or as protective coatings for woven goods.

Plastics and Ceramics: Plastics have fulfilled unusual functions in the ceramics field. Adhesives and impregnants are well known in their ability to improve water resistance, reduce porosity, and improve mechanical strength. Less known are the applications of organic plastics as temporary forming members for fine details such as threads in ceramics, the plastic disappearing during the firing operation used to cure the ceramic. Small amounts of certain plastics are important to the entrainment of air in Portland cement, while others establish moisture barriers on the surface.

Plastics and Explosives: In the development of explosives and rocket propellants, certain plastics have been important as binders for the oxidizers. The dividing line between nitrocellulose for plastics and nitrocellulose for explosives is rather narrow. Applying their own qualities of castability and extrudability to explosives, plastics have been used in making rockets. Better known are their applications as rocket launching tubes on aircraft. It is also probable that nitrated polymers will play a more important role in the explosives field.

Plastics and Metals: In the rise of organic plastics it was only natural that metal products should be thrown into competition with plastics products. When the best qualities of both materials are understood, designers find no difficulty in producing designs utilizing complementary features of both metals and plastics. While for the time of national emergency plastics were adopted as substitutes for more critical metals, this was only a temporary measure because both plastics and metals became critical materials. Today many metal fabricating concerns show their foresight by establishing a plastics department, whose responsibility is to see that both materials are used in their proper place. Only the uninitiated or the inexperienced fail to weigh properly the engineering properties of plastics. The fact remains that thus far there is no organic plastic made which can rival:

1. Surface hardness of metals
2. High modulus of elasticity of metals
3. Temperature resistance of metals
4. Strength of ferrous metals per unit area.

On the other hand, plastics owe much of their appeal to the following qualities:

1. Imperviousness to general chemical and atmospheric attack
2. Lightness in weight
3. Ease of moldability to complicated designs
4. Attractiveness and decorativeness
5. Pleasantness of touch due to favorable thermal properties
6. Combination of good electrical insulation with good mechanical strength.

Plastics as Decorative Material: One of the paramount reasons for the popularity of plastics is the attractiveness of the color schemes obtainable through the inclusion of the proper dyes and pigments. An almost unlimited variety of color combinations is available to suit every purpose, both in molded and laminated articles. The designer of products and machines cannot help but be color conscious, particularly when the consumer's own standards are being raised by colorful national advertising. Mottled colors, pearl essence effects, variegated colors, and many novelty effects can be skillfully worked into certain of the plastics. Ranging from dark, opaque shades to translucent and light pastels, plastics have done much to improve the color schemes of the appointments in automobiles and building interiors.

This first chapter has directed attention to the many branches of the plastics industry, and the many materials available to fulfill its many functions. From a careful examination of the engineering fundamentals of plastics in subsequent chapters, their value as engineering materials will be adjudged.

Chapter II

Types, Characteristics and Preparation of Organic Plastics

Organic plastics are so diversified in their nature and their origin that considerable attention has been given to their chemical background and the methods of classifying them. In covering the chemistry of organic plastics an effort is made to familiarize the reader with the basic materials from which the plastics are synthesized, at the same time outlining the processes by which useful engineering materials are prepared. Though no pretext is made of simulating the descriptive detail of the publications devoted solely to the preparation and processing of plastic materials, it is hoped that a survey of the chemical background will serve to dispel any hesitancy that an engineer may have in applying such materials. Several purposes are served by reviewing the chemistry of the plastic materials. In the first place, in the light of experiences with other engineering materials of construction, design engineers should feel better equipped to apply plastic materials if they have some working knowledge of how they are prepared and what limitations confront the materials manufacturers. Furthermore, a survey of this nature enables engineers to predict and to understand the variations in the properties of the plastic materials. In a later chapter, when the properties are analyzed, frequent references will be drawn to certain conditions in the preparations of the materials which contribute to the unusual behavior of some of them.

A plastic material is capable of being molded or shaped to some coherent form at some stage of its manufacture. Care was taken to state "at some stage of manufacture", for there are certain heat-hardenable plastics which can be molded only once, being converted to infusible substances by such operations. While plastic materials include inorganic as well as organic substances, this text deals primarily with those organic in nature, i.e., comprised of combinations of hydrogen, carbon, oxygen, and nitrogen. Inorganic materials such as clay or cement, while plastic in their behavior toward forming operations, are reviewed more adequately

in a paper devoted to ceramics. Another noteworthy exclusion from the classifications of organic plastic materials is natural rubber. In the past, activity in connection with the development and the application of natural rubber has concentrated upon the preparation of vulcanized, elastic materials. The fields served by such materials in general differ from those served by the plastics. However, the rubber industry and the plastics industry have certain features in common. In view of the recent success of organic plastics with rubber-like qualities, the two fields are running parallel along certain lines, with natural rubber products developed for their plastic qualities and certain plastics developed for their rubber-like properties, i.e., elastic qualities. In addition, recent synthetic rubbers employ large quantities of synthetic resins in their manufacture. Likewise some of the thermoplastics find synthetic rubbers useful as internal plasticizers.

The most convenient way of classifying organic plastics is in accordance with their response to thermal influences. All plastics may quite satisfactorily be described as being either thermoplastic or thermosetting.

Thermoplastic: A thermoplastic material usually is rigid at normal temperatures, but will soften upon the application of heat and deform under pressure.

Thermosetting: A thermosetting material will undergo chemical and physical changes under the influence of heat or catalysts to become substantially infusible and insoluble. The thermosetting plastics sometimes are referred to as heat-hardenable materials, and include such substances as phenolic plastics, urea plastics, alkyds and other groups outlined more completely in TABLE I.

Certain of the numerous organic plastics may be said to be on the borderline insofar as definitions of thermoplastic or thermosetting are concerned. These include some materials which revert to a thermosetting structure only after long periods of heating. There are others which may be classified as partial thermosetting materials because of the presence of infrequent cross linkages which may tie together an otherwise thermoplastic structure. However, in the majority of cases, thermoplasticity may be exhibited by thermosetting materials if they are reheated to temperatures appreciably higher than those at which they were formed.

Types of Plastics

Organic plastics may be prepared literally from hundreds of substances. Chemical literature is replete with research and data upon substances which constitute potential sources for plastics materials. From these, relatively few have been developed as commercially important materials. Those which have been developed for engineering purposes have combined economic feasibility with an optimum set of properties. There is no single plastic or group of plastics which is outstanding in all engineering requirements. Each one has advantages as well as limitations. Before undertaking an analysis of the various plastics in the light of their engineering characteristics, a survey will be made of the types of plastics, the raw materials employed in their manufacture, and a brief outline of their preparation. One of the most convenient ways of classifying plastics is in accordance with their source, and their thermoplastic or thermosetting behavior.

TABLE I presents an outline of the types of organic plastics. Four major groups are present with the synthetic resins serving as the most prolific source, followed by the cellulose derivatives, natural resins, and protein substances. It is always desirable to define the various group headings appearing in TABLE I. One of the most difficult is the synthetic resin by reason of the many shapes and uses it may assume. From liquids to infusible solids, or impregnants to molded articles, the synthetic resins are the most versatile of the materials. Capable of chemical readjustments to develop certain qualities, they sometimes are referred to as 'tailor-made' materials.

Synthetic Resin: A complex, substantially amorphous compound or viscous liquid, built up by chemical reactions between primary, non-resinous substances and capable of developing high molecular weights by processes of polymerization. In the polymerized form synthetic resin may be given physical characteristics which will lend it to the molding and fabrication processes of the plastics industry.

Cellulose Derivative: A natural-occurring high-molecular-weight polymer, comprising substantially a cellulose structure, which has been modified chemically to develop certain mechanical or chemical properties.

Natural Resin: A complex, substantially amorphous com-

TABLE I

Classification of Plastic Materials

Types	Major Fields of Application	Commercial Forms
SYNTHETIC RESINS (Thermosetting)		
Phenol-formaldehyde	Molding, laminating, casting, adhesives, impregnants	Molding powders, varnishes, liquid resins, laminated sheets
Urea-formaldehyde	Molding, laminating, adhesives, textile impregnants	Molding powders, varnishes, laminated sheets
Melamine-formaldehyde	Molding, laminating, adhesive, textile and paper impregnants	Molding powders, varnishes, laminated sheets
Phenol-furfuraldehyde	Molding and laminating	Molding powders, varnishes
Aniline-formaldehyde	Laminating	Varnishes
Alkyd resins	Surface coatings	Oil-soluble varnishes
Substituted phenol-formaldehyde	Surface coatings	Oil-soluble varnishes
Resorcinol-formaldehyde	Adhesives and laminating	Varnishes
Furfural-furfuryl alcohol	Adhesives and impregnants	Liquid resins
Polyester resins (including the allyls)	Low-pressure laminating and casting	Liquid resins and pastes
SYNTHETIC RESINS (Partial Thermosetting Qualities)		
Polyvinyl butyral (phenol-aldehyde modified)	Molding and coating	Molding powders and solutions
Styrene-divinyl benzene copolymer	Molding	Molding granules
Vulcanizable Copolymers Styrene-butadiene Acrylo-nitrile-butadiene Isobutylene-isoprene	Rubber industry	Sheets and finished goods
Vulcanizable polymer Chloroprene	Rubber industry	Sheets and finished goods
SYNTHETIC RESINS (Thermoplastic)		
Polymethacrylates	Molding and fabricating	Molding powders, transparent sheets
Polyamides	Molding and textiles	Molding powders, filaments, and woven goods
Polystyrene	Molding and fabricating	Molding powders, sheets
Polyvinyl chloride-acetate	Molding, laminating and fabricating	Molding powders, rigid and nonrigid sheets
Polyvinyl chloride	Rubber substitute and coatings	Lacquers and plasticized forms
Polyvinylidene chloride	Molding and textiles	Extruded tubings and woven goods
Polyvinyl formal	Molding (rubber-like)	Molding powders

TABLE I (*Continued*)

Types	Major Fields of Application	Commercial Forms
Polyvinyl butyral	Molding and coatings.	Molding powders, calendered sheets, safety glass
Polyvinyl acetate	Adhesives	Solutions and granules
Polyvinyl alcohol	Rubber substitute	Sheets and tubings
Polyethylene	Molding and extruding	Sheets and molding granules
Polyisobutylene	Rubber substitute	Liquids to semisolids
Silicones	Impregnants, oils, and coatings.	Varnishes and liquid resins
Maleic anhydride "adducts"-glycerol — fatty acids	Surface coatings	Liquids to semisolids
Polydichlorostyrene	Molding	Molding powders
Coumarone-indene	Extenders for coatings and varnishes	Liquids to solids
Polyterpenes	Extenders for coatings and varnishes	Semisolids to solids
Polytetrafluoroethylene	Chemical resistance	Films, rods, and tubes
CELLULOSE DERIVATIVES (Thermoplastic)		
Cellulose nitrate	Surface coatings and fabricating	Lacquers and sheets
Cellulose acetate	Molding and fabricating and textiles	Molding granules, thin sheets, woven goods
Cellulose acetate-butyrate	Molding and hot-melts for casting	Molding and casting solids
Ethylcellulose	Molding, fabricating, hot-melts	Molding powders, sheets, and solids for casting
Cellulose propionate	Molding	Molding compositions
Methyl cellulose	Coatings and thickening agent	Powders
Benzyl cellulose	Molding	Molding powders
Sodium carboxymethyl cellulose	Coatings	Aqueous solutions, powders
Regenerated cellulose	Packaging and textiles	Thin sheets and woven goods
Cellulose acetate-propionate	Coatings and Molding	Lacquers and molding compositions
NATURAL RESINS AND RUBBERS AND THEIR DERIVATIVES		
Shellac	Coating, molded parts, adhesives	Molding powders and solutions
Bitumen	Impregnant, adhesive, paving, molding	Semisolid to solids, molding compounds
Copal gum	Varnishes	Solids
Dammar gum	Varnishes	Solids

TABLE I (*Concluded*)

Types	Major Fields of Application	Commercial Forms
Arabic gum	Adhesives and sizings	Solutions
Lignin	Extender and laminating	Extender for phenolics, and laminated sheets
Gasoline-insoluble pine wood resin	Laminating and extender	Tubes and rods, extender for phenolics
Starch and starch esters	Adhesives and sizing agents	Powders
Rosin	Varnishes and sizing agents	Solids
Rosin esters (glycerol, pentaerythritol, glycols)	Coatings, adhesives and plasticizers	Liquids to semisolids
Hydrogenated rosin and esters	Coatings, adhesives, plasticizers	Liquids to semisolids
Polymerized rosin and esters	Coatings, adhesives, plasticizers	Liquids to semisolids
Chlorinated rubber	Acid-proof coatings, adhesives	Powders
Isomerized rubber	Adhesives	Powders
Rubber hydrochloride	Packaging and coatings	Thin sheets
PROTEIN SUBSTANCES		
Casein	Fabricating, sizing agent, adhesives, textiles	Powders, sheet, solutions, woven goods
Soya bean protein	Adhesives and textiles	Solutions and woven goods
Zein (corn protein)	Coatings	Powders and solutions
Blood albumin	Adhesives	Powders and solutions

pound or viscous liquid, occurring as a by-product of animal, vegetable, or marine life and having physical and chemical aspects similar to the synthetic resins.

Protein Substance: Natural-occurring high-molecular-weight polymers of widely differing chemical natures, either fibrous or nonfibrous in physical appearance and, on hydrolysis breaking down to a mixture of amino acids.

These classifications are presented herein largely on the basis of the chemical origin of plastics. Later, further distinctions will be made on the basis of their physical appearance and mechanical properties. With the exception of the natural resins, the organic plastics generally are of high molecular weight in their applied form. The development of this high-molecular-weight structure and the methods of modifying high-molecular-weight materials are the very essence of plastics chemistry. The results are in-

timately associated with the mechanical, thermal, chemical, and electrical behavior of the material.

Molecular Structures of Thermosetting and Thermoplastic Materials

The study of organic plastic materials is a study of high-molecular-weight compounds. It is not an easy matter to comprehend the structure of large-molecular-weight substances, though an analysis of the reactions leading to their formulation should be helpful in understanding their properties. Polymerization has been conceived as intermolecular combinations of similar materials, proceeding indefinitely to form larger complex molecules. Condensation phenomena proceed in a somewhat similar manner, with the exception that simple substances such as water are eliminated as by-products at the union of the molecules. There are two principal patterns which are followed in the formation of large, complex molecules.

In one of the patterns the molecules exist in the form of long, thread-like members. These long-chain molecules are characteristic of thermoplastic materials. They may be oriented so that their major axes lie parallel (greatest physical strength is developed under this condition) or they may be unoriented. On the other hand, a considerably more complicated structure exists for thermosetting materials, in which cross-linking between molecules occurs frequently. This three-dimensional structure explains the resistance of thermosetting materials to deformation by heat and resistance to swelling by solvents.

1. Chain-like Structure: In this pattern the molecules are joined end to end in a thread-like or chain-wise structure. Carbon to carbon linkages are the most common, though oxygen, nitrogen, and silicon linkages may prevail. Some of the long-chain molecules exhibit crystallinity when stretched. The growth of the long-chain molecule may take place as a simple additive polymerization, which occurs, for example, on opening of the double bonds of a vinyl resin, symbolically represented as:

nR — polymerizes to — (-R-R-R-R- . . . . . -R-R-)n

Where R may be, for example $CH_2 = CHX$, and X a halogen, alkyl, or aryl group.

Long-chain molecules may also grow through condensation-polymerization phenomena of bifunctional molecules; for example, ethylene glycol and sebacic acid, symbolically represented as:

$$nR_1^1 + nR_2^1 \text{ — polymerize to} \rightarrow$$
$$(\text{-}R_1\text{-}R_2\text{-}R_1\text{-}R_1\text{-}\ldots\ldots\text{-}R_1\text{-}R_2\text{-})n + nH_2O$$

where R_1^1 is a dihydric alcohol (containing 2 alcohol groups) and R_2^1 is a dibasic acid (containing 2 acid groups).

An additive polymerization to form a chain-like structure may also occur between dissimilar molecules, each possessing double bonds, leading to what is known as copolymerization. This may occur between two or more molecules and may be symbolically illustrated as follows:

nS and nR — polymerize to — (-S-R-S-R- . . . . . -S-R-)n or combinations thereof

The chain-like structure is the basis of the thermoplastic material, strong primary bonds between members of the chain, and weaker secondary forces between adjacent chains. Polymerization is concerned more with reactions betwen molecules, and less between atoms to form a molecule, than are inorganic and organic chemistry. *Fig.* 2 illustrates graphically the formation of long-chain molecules through the interaction of simple molecules. The final state, fully polymerized thermoplastic synthetic resin is now ready for incorporation in molding compositions, cements, surface coatings, etc. This reaction is illustrative of the formation of polystyrene, polyacrylic, and certain polyvinyl resins.

2. Complex 3-Dimensional Structures: By processes of condensation-polymerization, addition polymerization or combinations of both, certain molecules are not only capable of reacting with one another to form a chain-like structure, but also across the chains to form a three-dimensional cross-linked structure. This type of molecular growth is typical of the thermosetting resins, and serves to explain the relative infusibility and insolubility of such materials, when polymerized to their fullest extent. The conception of the 3-dimensional structure will be useful in interpreting the physical properties of the phenolic plastics in a later chapter.

A useful schematic illustration, *Fig.* 3, of the structural changes ensuing in thermosetting resins has been conceived by Dr.

R. Houwink*, in which the simultaneous existence of soluble and insoluble units is deemed a possibility. The transformation from a soluble, fusible stage A heat-hardenable resin to a stage C infusible, insoluble material is depicted herewith. In understanding the theoretical background to this illustration, one must recognize that the atoms have lost their singularity. Further, a dis-

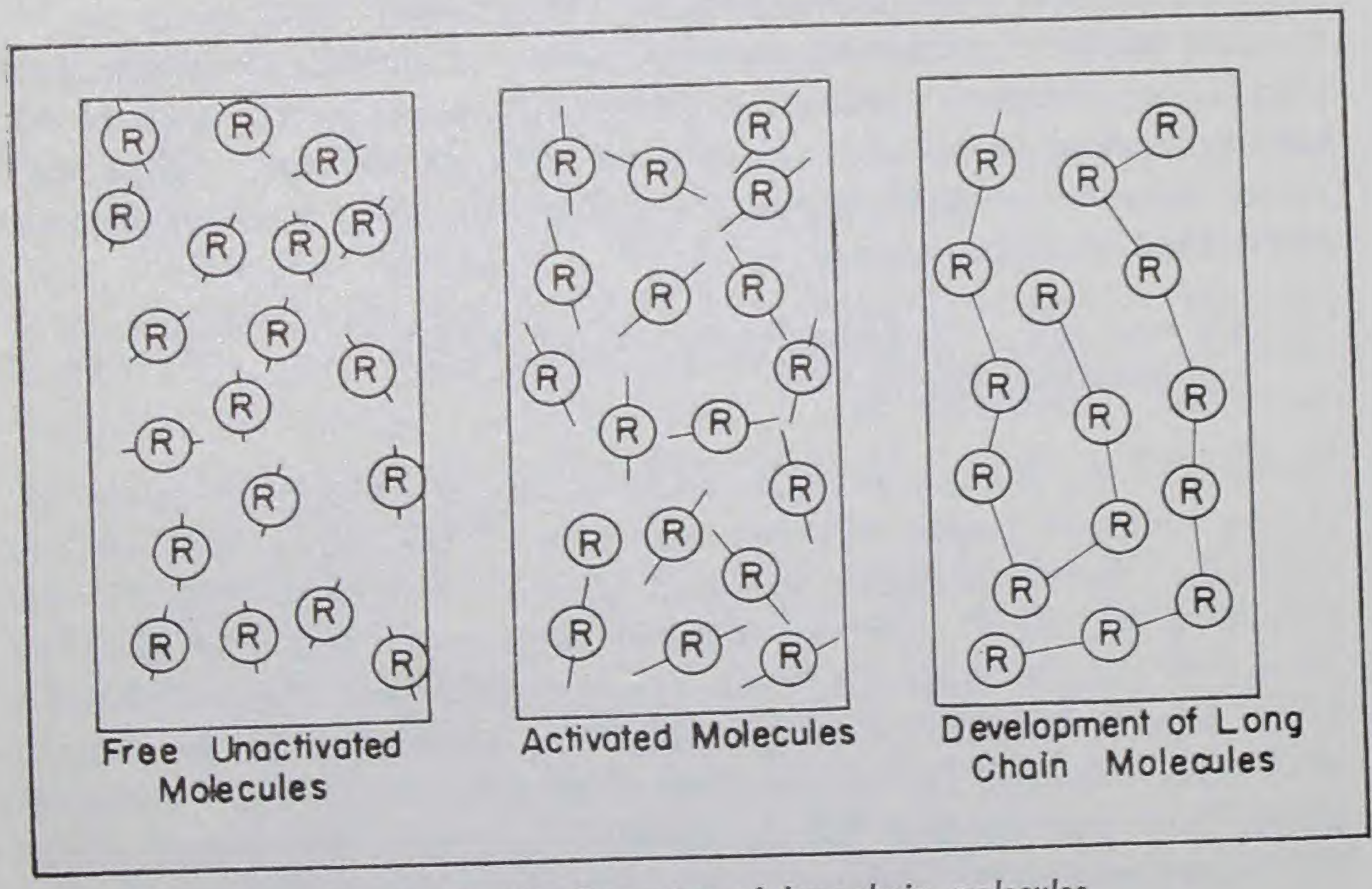
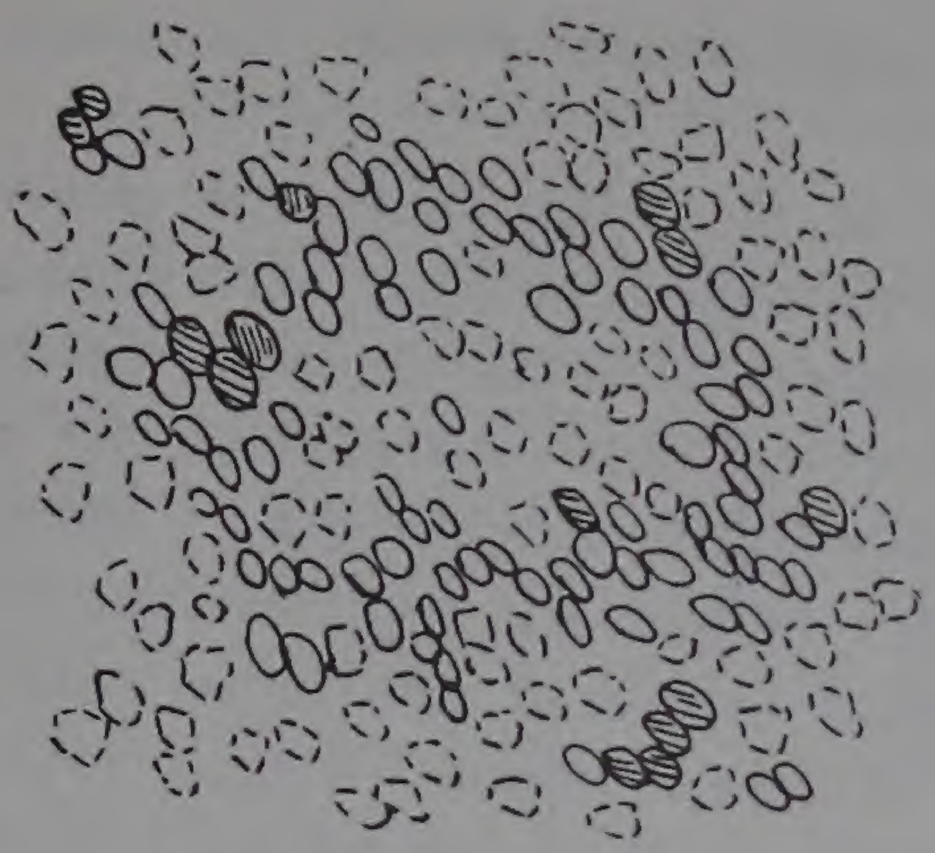


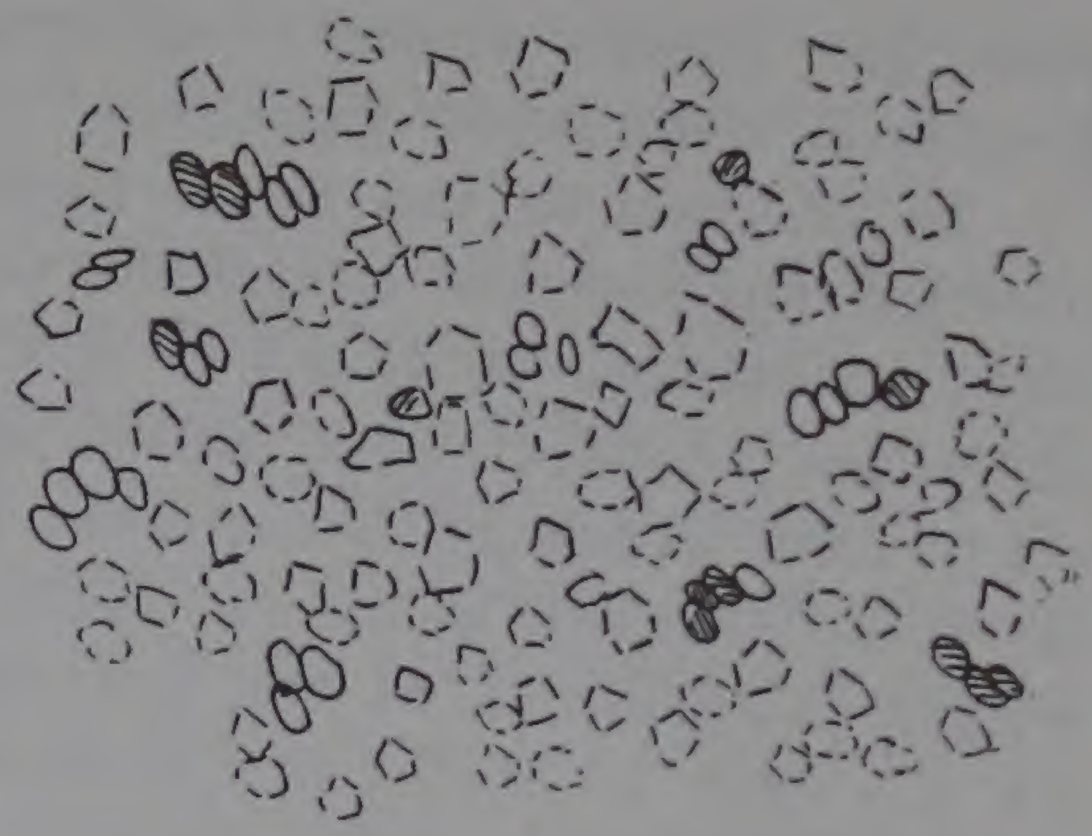
Fig. 2—Graphic formation of long-chain molecules

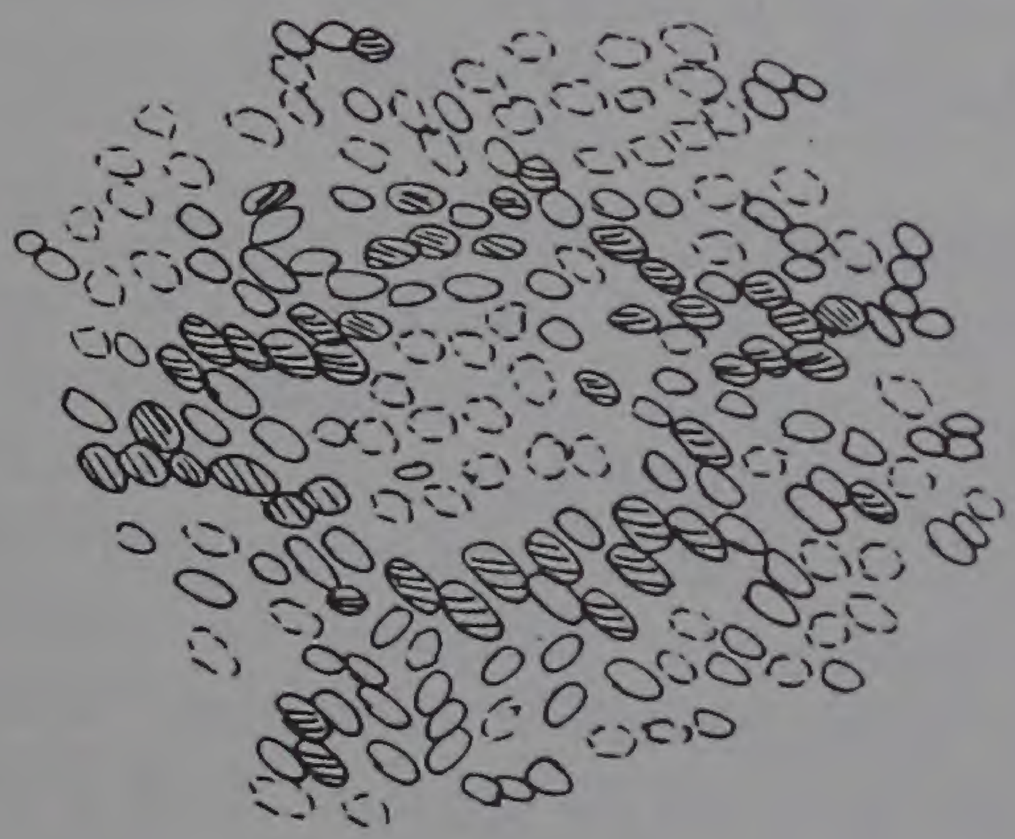
tinction may be made between intermolecular cohesive forces on the basis of the energy content of the bonds, primary bonds being considerably stronger than secondary bonds.

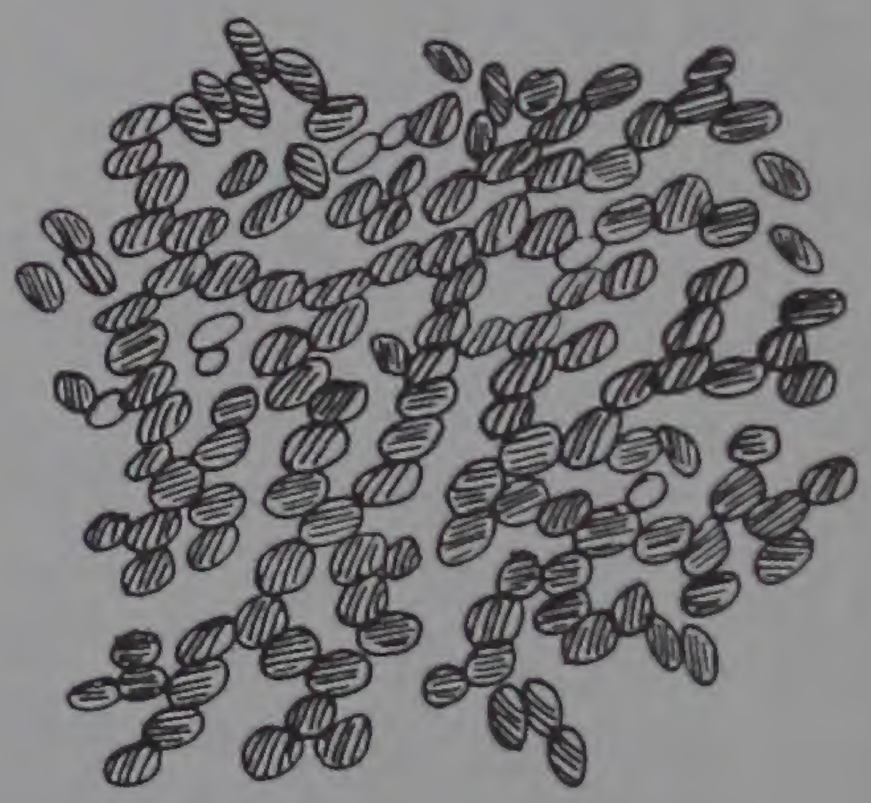
As a thermosetting resin (or thermoplastic resin) polymerizes, primary homopolar bonds are formed where valence electrons of adjacent molecules are shared mutually at the reactive points of the molecules. Intermolecular secondary bonds also will be formed because of the electrostatic forces of attraction between dipole, induced dipole, and ionic charge combinations. When the secondary forces prevail, the molecule still is fusible and soluble. However, in stage B of the thermosetting resins, or a thermosetting

*Elasticity, Plasticity and Structure of Matter, By R. Houwink, Cambridge University Press, London, 1937.









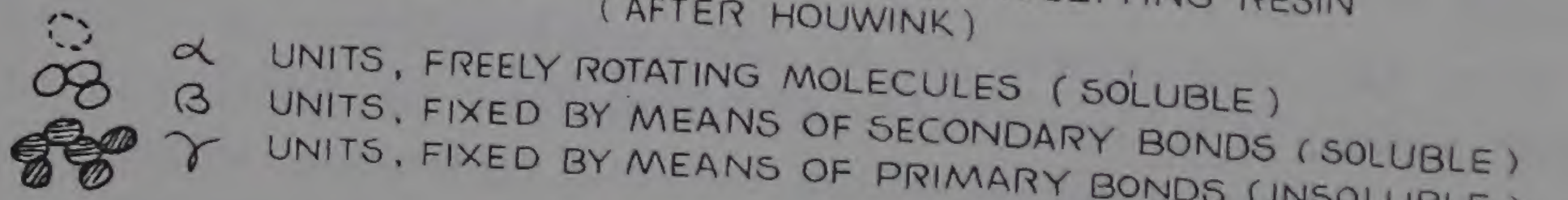


Fig. 3—Schematic diagram of structural changes in thermosetting resins

resin not fully polymerized, there is a possibility that groups of molecules cohering by secondary forces may be entrapped by an encirclement of primary bond linkages. Thus those elements still will be susceptible to attack by solvents, though the structure is essentially nonfusible. Full polymerization of thermosetting resins witnesses substantial establishment of primary bond linkages between adjacent molecules. However, only a small portion of the theoretically possible linkages is established. Calculations show

that the tensile strength of synthetic resins would be much greater if these were completed.

In addition to the isogel theory of Houwink there are other theories particularly adaptable to the thermosetting structures. Most prominent of these is the sphero-colloidal theory, which visualizes small clumps, called sphero-colloids, distributed in a continuous phase of lower-molecular-weight components.* Both theories, however, admit the possibility of low and high-molecular-weight components in the polymerized or cured synthetic resin. As the cure advances the number of low-molecular-weight components disappear, and resistance increases in chemical tests such as those based upon the extraction of soluble constituents. However, as the cure continues, the rate of polymerization decreases and the presence of traces of unpolymerized fractions is always theoretically possible.

The presence of high and low-molecular-weight fractions prevails not only for the thermosetting synthetic resins but also for the thermoplastic synthetic resins as well as the cellulose derivatives. While the non-uniform molecule weight may at first appear to be a disadvantage, it has its merits from a processing point of view because it permits proper balance of polymers to obtain good molding or good solubility characteristics consistent with good physical qualities. Expressed in a simple manner, it is possible to soften or plasticize a high-average-molecular-weight compound with a lower-molecular-weight fraction of the very same material.

With the appearance of an increasing number of thermosetting resins, it is becoming more important to distinguish between the degree of cross-linking between molecules, which phenomenon establishes a thermosetting material. Infusibility and insolubility may at times arise from one or a combination of the following:

(a) Molecules which of themselves are capable of cross-linking to one another (this is expressed in terms of certain unsaturated molecules with conjugated double bonds; in terms of poly-functionality; or simply, reactive points on the molecule)

(b) Added substances capable of bridging the molecules and establishing primary bonds (such as vulcanizing agents in rubber manufacture)

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*H. Stager, W. Siegfried and R. Sanger—Helv. Phys. Acta.—12, 561, 1939.

(c) Absorption of gases, particularly oxygen, capable of rendering certain resins or polymerizable oils infusible and insoluble.

A large measure of control is possible through the first alternative noted above. This art has been particularly evident in the manufacture of the new polyester resins, described later in this chapter, wherein numerous unsaturated alcohols and acids can be reacted together to form a thermosetting structure. Also significant is the control over the time at which cross-linking is established. When initiated too early in the course of polymerization, a brittle type of polymer is formed, though at the correct time, a tougher, more elastic polymer ensues. As also may be surmised, the less the number of cross-linkages the more thermoplastic the polymer. For these reasons, the partial thermosetting synthetic resins listed in TABLE I have been set off from the more brittle type of thermosetting resins.

In discussions so far the organic plastic has been portrayed as an amorphous material. Its film forming qualities, random molecular weight distribution, and indefinite melting point range suggest this classification. However, there is some recent evidence that for some of the materials, there exists crystalline regions, where long-chain molecules may be grouped together in orderly patterns, accompanied by amorphous regions and random separations of these molecules. Under certain processing and manufacturing techniques, the presence of discrete spots can be observed in X-ray diffraction photographs indicating the presence of crystalline groupings.

The following definitions are tabulated for the convenience of the reader:

POLYMERIZATION: A chemical change resulting in the formation of a new compound whose molecular weight is a multiple of the original substance.

CONDENSATION-POLYMERIZATION: The union of molecules accompanied by the elimination of water or simple by-products to form large complex molecules which are multiples of the original molecules less the by-products.

MONOMER: An unpolymerized molecule, capable of conversion to larger molecules (as, for example, through an additive polymerization).

POLYMER: Multiples of the monomer, or compounds with the same proportionate composition of elements.

Methods of Polymerization

The methods of polymerization depend upon the type of end product which is desired and the manner in which it is to be used. Polymerization is usually effected by *heat* or *catalysts* or sometimes both. Catalysts may be chemical in nature or dependent upon the influence of ultraviolet light. When polymerization takes place it may be conducted as:

(a) MASS POLYMERIZATIONS: Resin monomer is cured to a solid block or sheet, or polymerized 'in situ' after impregnating a porous material.

(b) SOLUTION POLYMERIZATION: The resin monomer is dissolved in an appropriate solvent from which it may precipitate as it is polymerized, or remain in solution. The molecular weight is dependent upon the solvent. Some vinyls are polymerized in this manner.

(c) EMULSION POLYMERIZATION: In the manufacture of molding granules or special coatings, the resin may be polymerized in an emulsion with the aid of appropriate catalysts and emulsifying agents.

Conditions of Polymerization: Organic substances which are susceptible to condensation and polymerization reactions presuppose the existence of highly reactive points in the individual molecules, at which points the primary valence bonds take effect in forming the links between adjacent molecules. In connection with the formation of polymers, there are three interesting postulates established by Kienle in his investigations on alkyd resins*. These postulates are listed herewith:

I. Organic compounds of a high molecular weight are formed only when the interacting molecules have more than one reactive point apiece.

II. Interlinking of molecules proceeds according to chance contact of two reactive points.

III. The relative size and shape of the reacting molecules and the position of the reactive points on the molecule largely determine the physical properties of the resulting substances such as hardness, flexibility, heat convertibility, etc.

The dependence of physical, chemical, and electrical properties upon the nature of the polymer formed cannot be emphasized too strongly. In a subsequent chapter on the properties of plastics, relationships will be drawn between physical properties and

*R. H. Kienle—*Jl. A.C.S.*—55, 228-T, 1936.

the molecular weight. Aside from the basic aspects of polymerization, there are the possibilities of co-polymerization, whereby two or more monomers are combined in varying proportions to achieve a structure different in physical and chemical characteristics from either one of the components by themselves. While there are two or three striking examples of commercial copolymers (polyvinyl chloride-acetate, polyvinyl chloride-polyvinylidene chloride, and polyisobutylene-isoprene being the most prominent), the field of copolymerization is still relatively new and the possibilities without limit. It may only take a small percentage of a second component to change profoundly the characteristics of the initial reagent. For example, copolymerization of a small amount of divinyl benzene (which has four reactive points) with styrene will form a polymer of much greater solvent resistance and heat resistance. Or still another approach is indicated in the example of isobutylene copolymerized with a few per cent of isoprene. The polyisobutylene by itself forms a linear polymer which is substantially unsaturated and incapable of vulcanization or cross-linking. The inclusion of a small amount of isoprene admits a reactive, unsaturated portion into the linear polymer, which the vulcanizing ingredients can influence.

Through the processes of copolymerization it is possible to introduce side groupings into a polymer and predetermine the physical and chemical aspects of the final molecule, though additional complications may be introduced due to the influence upon the rate and the degree of polymerization by the side groupings. The elastic properties, the temperature resistance, the influence of solvents, and the dielectric constant, for example, are dependent upon the identity of the side groupings which are attached to the long chain-like molecule.

Methods of Altering Properties of the Polymer

In the discussion so far, a few of the principles underlying the control of polymerization have been cited, particularly with reference to the selection of the starting materials. In addition to this there are numerous circumstances where changes may be made on the final polymer to develop certain characteristics. This technique is indispensable to the natural high polymers, which seldom are found in nature in a form usable or adaptable to our

engineering requirements. The entire background of cellulose derivatives is predicated upon reactions at the available hydroxyl groups, which introduces side groupings possessing desirable qualities of moldability or solvency. No further polymerization takes place and, if anything, a degradation occurs, though in the end a useful high polymer is obtained. The chemical grouping accompanying the cellulose generally is identified in the nomenclature as, for example, cellulose *nitrate* or cellulose *acetate*.

At present there is considerable research being conducted upon chemical changes in other natural high polymers. Most notable of these are lignin and starch. Starch esters and lignin esters appear to offer materials which will play more prominent roles in the fields of plastics. Even the polymers prepared from synthetic resins are capable of undergoing further changes, striking examples of which appear in the aldehyde modified polyvinyl alcohol resins. Other examples include chlorination of the polymer, as for example after-chlorinated polyvinyl chloride, which appears to have better toleration of solvents than the straight polyvinyl chloride. Again the possibilities are limitless, as chemical treatments of the polymers have scarcely begun to be extensively explored.

At present the most widely used method of altering the properties of the polymer is to admix mechanically various proportions of plasticizing agents such as various natural resins or high-boiling-point esters to obtain a proper balance of moldability and good physical and chemical properties. The function of a plasticizer is primarily to soften a polymer so that it will be capable of being molded or extruded more readily. While plasticizers have their many advantages, they also introduce new limitations in imparting greater sensitivity to temperature changes, which works to advantage when molding at high temperatures, but to disadvantage at low temperatures, when the polymer-plasticizer combination becomes brittle more readily. Further problems of odor, taste, and exudation also are present with plasticizers.

Plasticizers generally are not effective in application to thermosetting resins except in only a temporary manner. Properties of thermosetting resins usually are controlled with the aid of various fillers. These have made possible the development of many industrially important compounds, and in the chapter to follow

the role played by fillers will be elaborated upon more completely.

Reactions of Phenols with Aldehydes

The wide variety of products derived from phenols and aldehydes is readily apparent from the summary in TABLE II. Of the reagents, the two most widely used are phenol and formaldehyde, though the products of all of them are referred to generally as

TABLE II

Phenol-Aldehyde Resins

Raw Materials

Coal tar, benzol, methyl (wood) alcohol, oat hulls

Reagents

Phenol, cresols, xylenols, resorcinol, substituted and modified phenols, formaldehyde, furfuraldehyde (furfural)

Products	Typical Applications and Trade-names
LOW - MOLECULAR - WEIGHT RESINS (water-soluble)	Resin impregnation of wood and other cellulosic structures
MEDIUM-MOLECULAR-WEIGHT RESINS (partially polymerized)	
Solid, fusible types compounded with catalysts, pigments, fillers, lubricants	Molding compounds ("Durez", "Bakelite", "Makalot", "Resinox")
Solutions in alcohol	Laminating compounds
Resin solutions or powders plus separate catalysts	Adhesives
100 per cent liquid resins plus separate catalysts	Casting resins
Special liquid varnish resins cooked with drying oils	Surface coatings
HIGH - MOLECULAR - WEIGHT RESINS (fully polymerized)	
Laminated sheets, rods, tubes and miscellaneous forms	"Textolite", "Insurok", "Micarta" "Synthane"
Molded articles	
Cast sheets, rods, tubes, and miscellaneous forms	

phenolic plastics. The various stages of resinification are sometimes distinguished by letter symbols, originally suggested by Dr. L. Baekeland. These are as follows:

Stage "A" resins—fusible and soluble
Stage "B" resins—fusible and soluble with difficulty
Stage "C" resins—infusible and insoluble.

These designations, however, are falling into disuse, largely because of the difficulty of defining exactly when stage "A" ends and stage "B" commences. Regarding stage "C", there is no question when this stage is attained, subject, however, to fur-

ther thermoplasticity as explained in the definition of thermosetting materials earlier in this chapter.

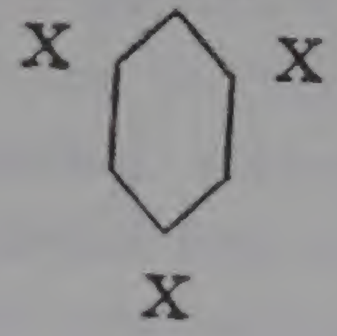
The properties which are to be developed in the final products govern the selection of the initial starting reagents. Phenols, generally defined as hydroxyl derivatives of aromatic hydrocarbons, consist of many types, some of which are highly reactive, others of which are relatively sluggish. The more reactive members are pure phenol, meta-cresol, 3,5 xylenol, and resorcinol, the last two members showing the highest reactivity of all. Ortho and para-cresol and a number of xylenols also may be present in the starting reagents though these react less rapidly with formaldehyde, tending to yield resins with poor thermosetting qualities. However, they are significant in that by proper balancing of the slowly reactive materials with the more reactive types, fast and slow curing resins may be developed. Fast curing types are desirable for small, thin-walled molded articles, while slower curing types are necessary for thick molded parts requiring long flow, or in the laminating of cloth and paper into thick sheets.

Mixtures of phenol, cresols, and xylenols are known commercially as cresylic acid. Technical grades of phenol derived from coal tar may contain 80-95 per cent phenol, while purer grades are derived upon synthesis from benzol. Lighter color resins are derived from pure phenol, whereas cresylic acid mixtures will yield dark, brown products. Synthetic phenol is used more widely than any other reagent.

Among the aldehydes, formaldehyde is the most widely used and the lowest in cost. It is prepared by the catalytic oxidation of methyl alcohol and is available commercially as formalin, a 37 per cent solution of formaldehyde (a gas) in water. Polymers of formaldehyde, as for example, paraformaldehyde, are available as finely divided white powders and are reacted with phenol-formaldehyde condensation products as a catalyst, or else with reagent phenol when it is desired to reduce the quantity of water to be removed from the resin. Furfural is also reacted with phenols to form the phenol-furfural plastics, which resemble the phenol-formaldehydes in many respects. In fact both furfural and formaldehyde may be employed together in reactions with the phenols.

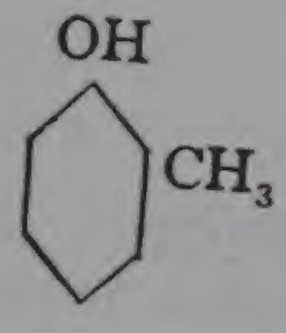
Before outlining the nature of the condensation-polymerization reactions of phenols with formaldehyde, a study must be made of those points in the phenol molecule which are regarded as *reactive*

points. For example, in the following chemical notation for phenol (C_6H_5OH), an X is placed at those positions of the benzene ring at which methylene linkages may be established in the interlinking of the molecules during condensation-polymerization.

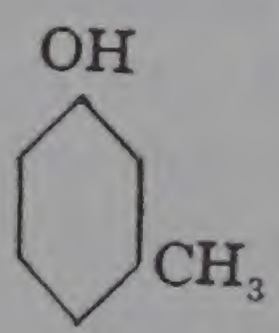


Phenol

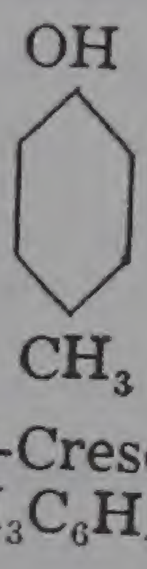
In the case of ortho and para-cresol, one of the reactive points may be saturated by the presence of a methyl group, while meta-cresol still possesses three potentially reactive points. The notations for these isomers are as follows:



O-Cresol
$CH_3C_6H_4OH$

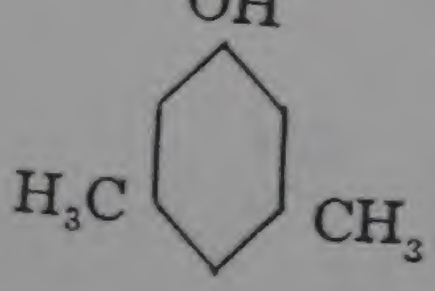


M-Cresol
$CH_3C_6H_4OH$

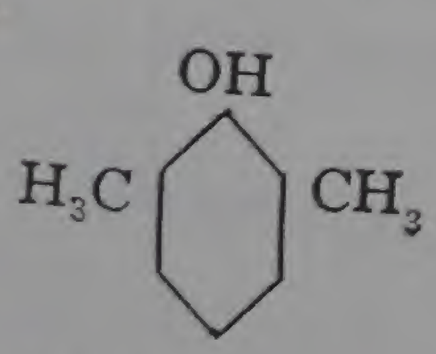


P-Cresol
$CH_3C_6H_4OH$

With the exception of 3,5 xylenol, the xylenols are relatively less active in resinification due to the saturation of reactive points with methyl groups. An example of a poorly reactive compound is 2,6 xylenol with only one reactive position. The chemical notations for these xylenols are as follows:



3,5 Xylenol



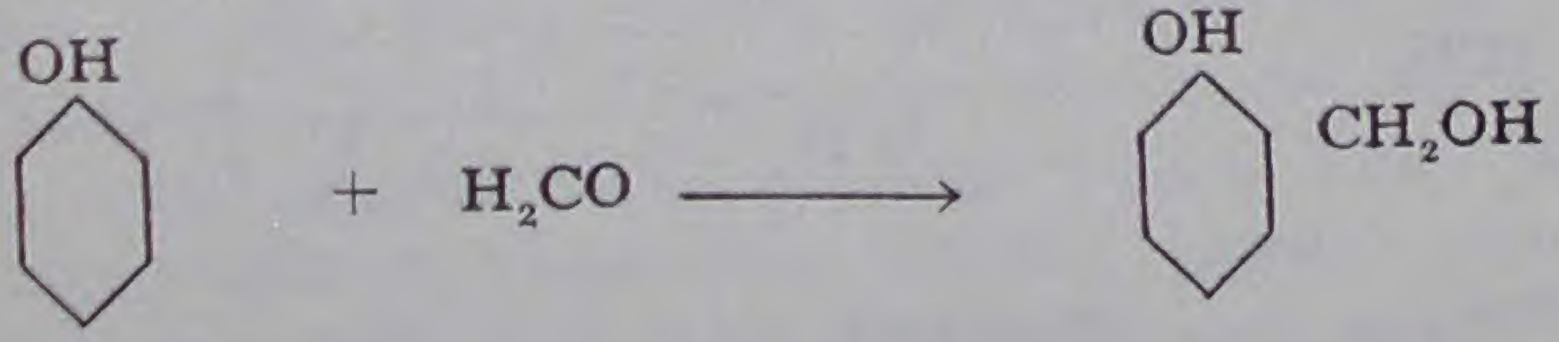
2,6 Xylenol

The significance of the reactive points on the phenol molecule assumes importance when it is pointed out that the materials which will resinify most readily are meta-cresol, phenol and

3,5 xylenol. On the other hand, reactions between ortho-cresol and formaldehyde proceed slowly in the formation of heat-hardenable resins. Resins prepared with a high proportion of ortho-cresol will have poor molding qualities.

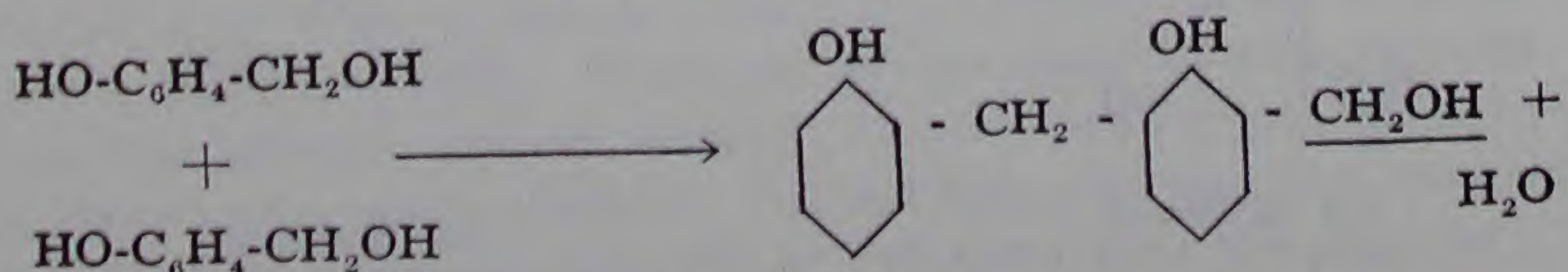
Commercial processes for preparing phenol-aldehydic resins are described as 1-stage wet processes or 2-stage wet processes. Their outstanding features are described in the following paragraphs:

1-Stage Wet Process: In the 1-stage wet process, equimolecular proportions of phenols and formaldehyde (or slight excess of aldehyde) are heated in the presence of an alkaline catalyst as NaOH. The formation of phenol alcohols takes place rapidly, whereby the formaldehyde molecules attach themselves at ortho or para positions with respect to the hydroxyl group. Attachment of aldehydes to more than one reactive point on the phenol molecule is possible, and dialcohols as well as a trialcohol may be formed. A typical reaction follows:



Phenol Formaldehyde - O-Hydroxy-Benzyl Alcohol

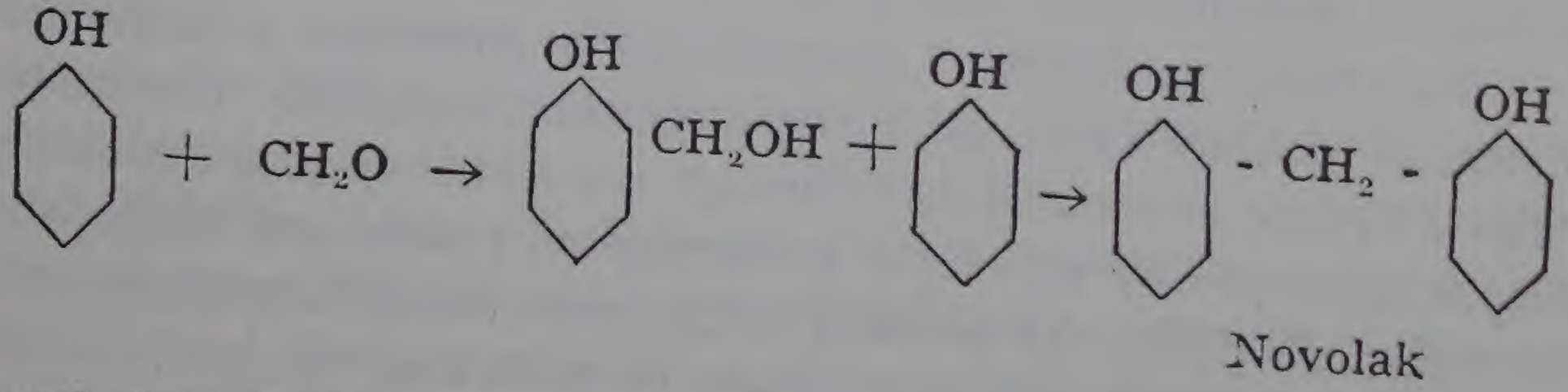
Though the reaction may be stopped at this point to yield a high proportion of phenol alcohols, commercial processes permit the reactions to continue which take place relatively slowly after the formation of the alcohols. Resinification proceeds as phenol alcohols condense with one another or with free phenol molecules. Two phenol alcohols will condense with one another to eliminate water and form diphenylomethane:



It should be noted that the CH_2OH group on the last formed molecule is underlined, to signify that this portion of the molecule is capable of further condensation with an H-atom of a re-

active point of the benzene ring, yielding water and establishing another intermolecular linkage, leading to the formation of high-molecular weight substances. Without going into further detail it should be noted that the less reactive phenols (such as cresylic acid mixtures) will not resinify as readily because of the fewer available reactive points. Inasmuch as the one-stage reaction entails the preparation of a phenolic resin which has a tendency to resinify rapidly, care must be taken in applying heat to the reaction. Thus for example, where it is necessary to heat the reagents, the time and temperature of application is carefully controlled. Water from the formalin and from condensation-polymerization reactions is preferably removed under vacuum at a temperature of 50 C (122 F). If precautions of this nature are not carried out, dehydration may bring about premature setting-up of the resin in the reaction kettle. After water has been removed by vacuum, sometimes aided by a decanting operation from the upper surface of the resin where it collects, the resin is poured into open trays to cool and harden. It is then broken up into lumps for further compounding. In this form it is still heat reactive (not fully polymerized). Full polymerization does not occur until the actual molding.

2-Stage Wet Process: Under the influence of a mineral acid catalyst and an excess of phenol over formaldehyde, a fusible product first is obtained. This fusible product is called a Novolak resin. The addition of further formaldehyde at a later stage, in the presence of a basic catalyst, will yield the heat-convertible stage "A" resin (see *Fig.* 4). In this process the formation of the phenol alcohols is not well defined as in the 1-stage process, inasmuch as reactions between monoalcohols and phenol proceed rapidly to the formation of a novolak resin. Inasmuch as there is



Novolak

much less tendency for this resin to set-up prematurely in the reaction kettle, dehydration may be carried out at higher temperatures before the resin is poured. Aldehydic catalysts such as

hexa are added to the resin after further compounding to convert it to a heat-hardenable form.

Hexa (hexamethylenetetramine) is a well known catalyst, prepared by the action of ammonia on formaldehyde. On heating it forms ammonia and makes available methylene linkages for bridg-

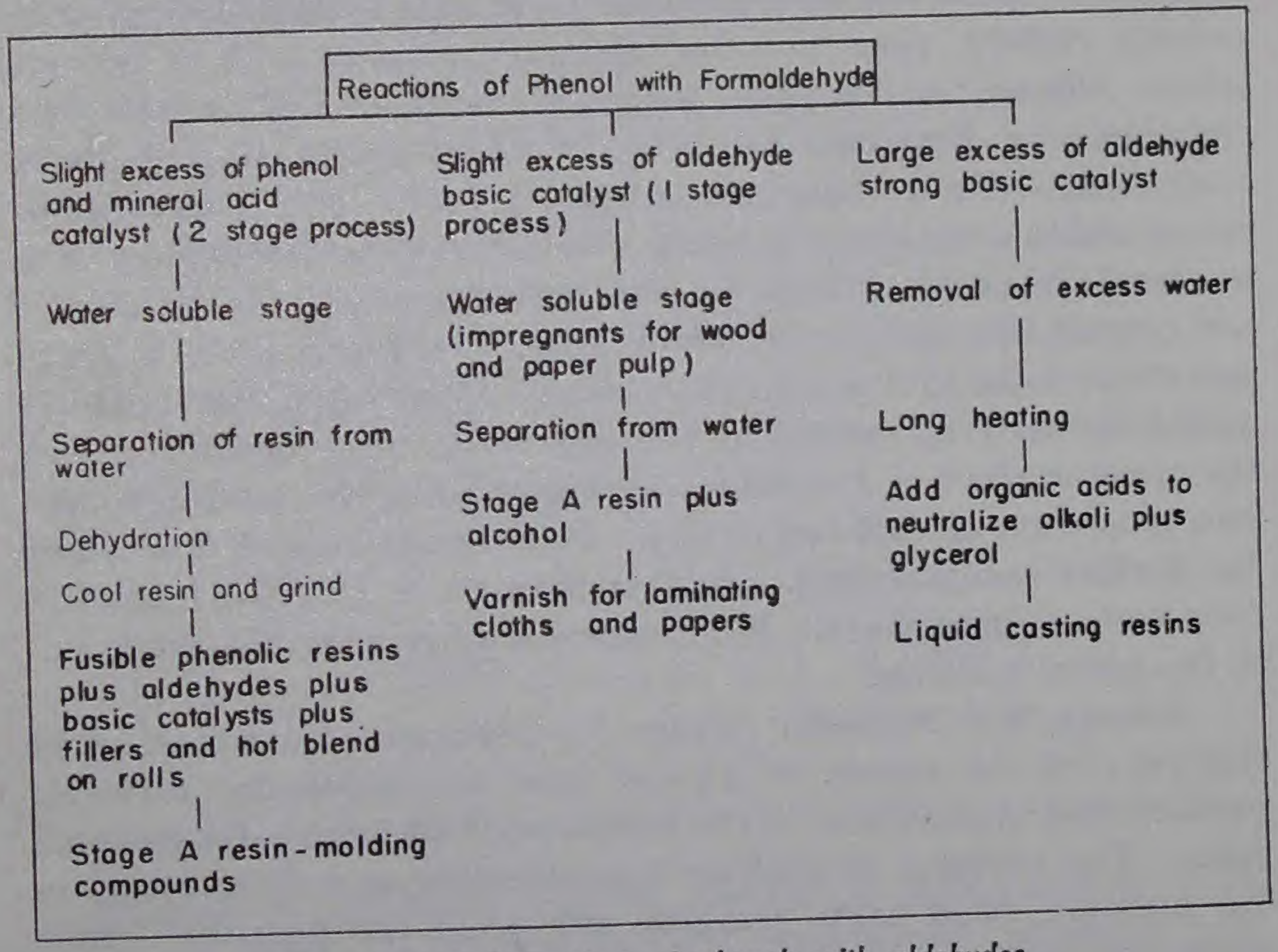
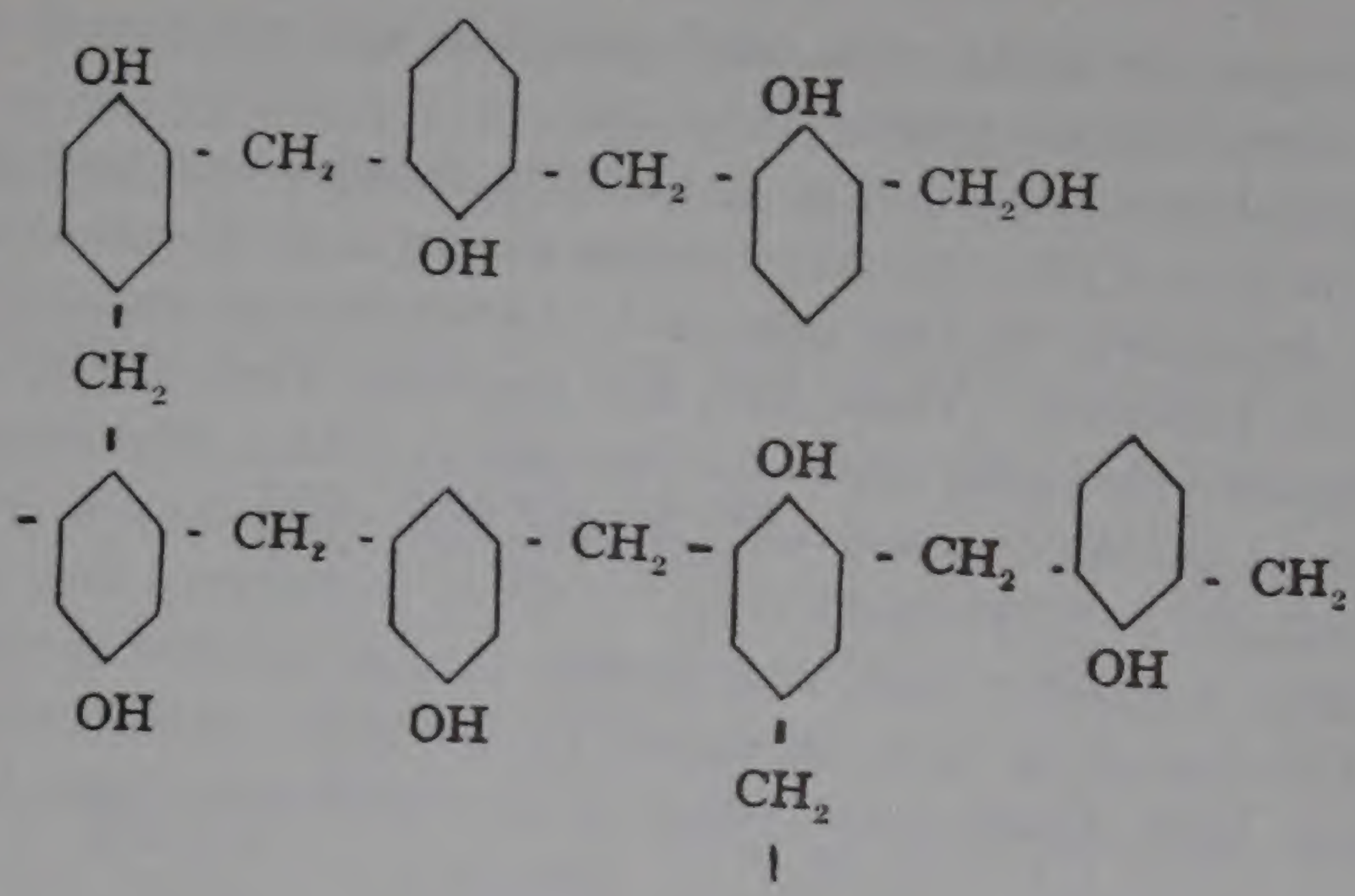


Fig. 4—Typical reactions of phenols with aldehydes

ing the phenolic molecules and establishing the thermosetting structure. The amount of hexa added is sufficient to give a molar excess of formaldehyde over phenol in the final product.

The fully polymerzied phenolic resin possesses a molecular structure characteristic of a thermosetting material. Intermolecular linkages are established through condensation-polymerization reactions, involving alternate groupings of phenol and methylene radicals. Further, the phenols with three reactive positions are capable of forming primary bonds, cross-linking to one another through the methylene groups (derived from formaldehyde). A small portion of the complex phenol-formaldehyde polymer is shown herewith:



These heterogeneous complex molecules form typical amorphous compounds. There is no well defined softening point, no evidence of crystallinity, and a very high molecular weight difficult to evaluate. Examination of X-ray diffraction photos shows a gradual blurring of the characteristic rings as polymerization proceeds. In the formation of this structure it is also conceivable how soluble, small polymers may be encircled by the formation of strong, primary cross-linkages between molecules. Even in the fully polymerized products such as molded or laminated articles, there is evidence to show that polymerization continues for some time, though at a much reduced rate. This is manifested by after-shrinkage of the product in service and through a gradual reduction of acetone extraction content.

Preparation of Phenolic Molding Compounds: Phenolic molding compounds are prepared by blending together various fillers, pigments and lubricants with the stage "A" type of resins, followed at the last by catalysts such as hexa. Fillers are added for numerous reasons. They not only reduce the amount of shrinkage in the molded parts, but often improve mechanical properties such as impact strength, or electrical properties such as lower loss factor. Color selection for the phenolics generally is limited, as the lighter shades have not generally proved light fast and will fade. While transparent, amber colored phenolics have been prepared, these too, will darken with the passage of time. The function of lubricants in molding compounds is to permit the molded article to release better from the hot mold and not stick.

Metallic soaps, carnauba wax, and graphite are commonly employed as lubricants for plastic materials.

A typical composition for a phenolic molding compound is tabulated in TABLE III. The proportions shown may be varied considerably depending on the uses and characteristics required of the finished products. There are, for example, clear amber colored phenolics containing no filler, and others with a high-density filler such as asbestos, where only 30 per cent resin may be present (by weight). Plasticizers may be added to improve flow during molding, a quality particularly desirous in transfer molding. Chlorinated diphenyls and cardanol (a phenolic constituent in cashew nut shell liquid) are among those which have been used.

TABLE III

Composition of a Typical Phenolic Molding Compound

Binder (including hardening agents)	45 to 50%
Coloring matter	up to 5%
Lubricants	up to 1%
Fillers (cellulosic)	40 to 45%
Plasticizers (in special cases)	up to 5%

In blending together the various ingredients two methods may be followed: Wet blending and dry blending. As the resin reaches the desired degree of polymerization in the kettle, and upon removal of substantially all of the water, it is flowed out of the kettle and allowed to solidify outside. Before blending with other ingredients it is broken up into lumps, convenient to handle. While a thorough penetration of the resin into the filler is obtained by blending in the presence of a solvent (wet blending), there is added the difficulty of adequately removing and recovering the solvent. Furthermore, better impact strength may be realized when the resin is adsorbed on the surface of the filler rather than into its structure.

Dry blending, illustrated in the flow chart in *Fig.* 5, is preferred for heat-reactive molding compositions. Ingredients are first mixed together at room temperature in a ball mill or hammer mill. This not only grinds them down to a size convenient for further handling, but also produces a substantially uniform mix of the varied materials, reducing the time required in further hot blending operations. Catalysts such as hexa may be introduced at this stage. Hot blending promotes uniform dispersion of the resin through the fillers and, at the same time, increases

the bulk density of the compound. The stage of cure of the resin is advanced further during hot blending, which must be short enough to prevent premature hardening of the resin.

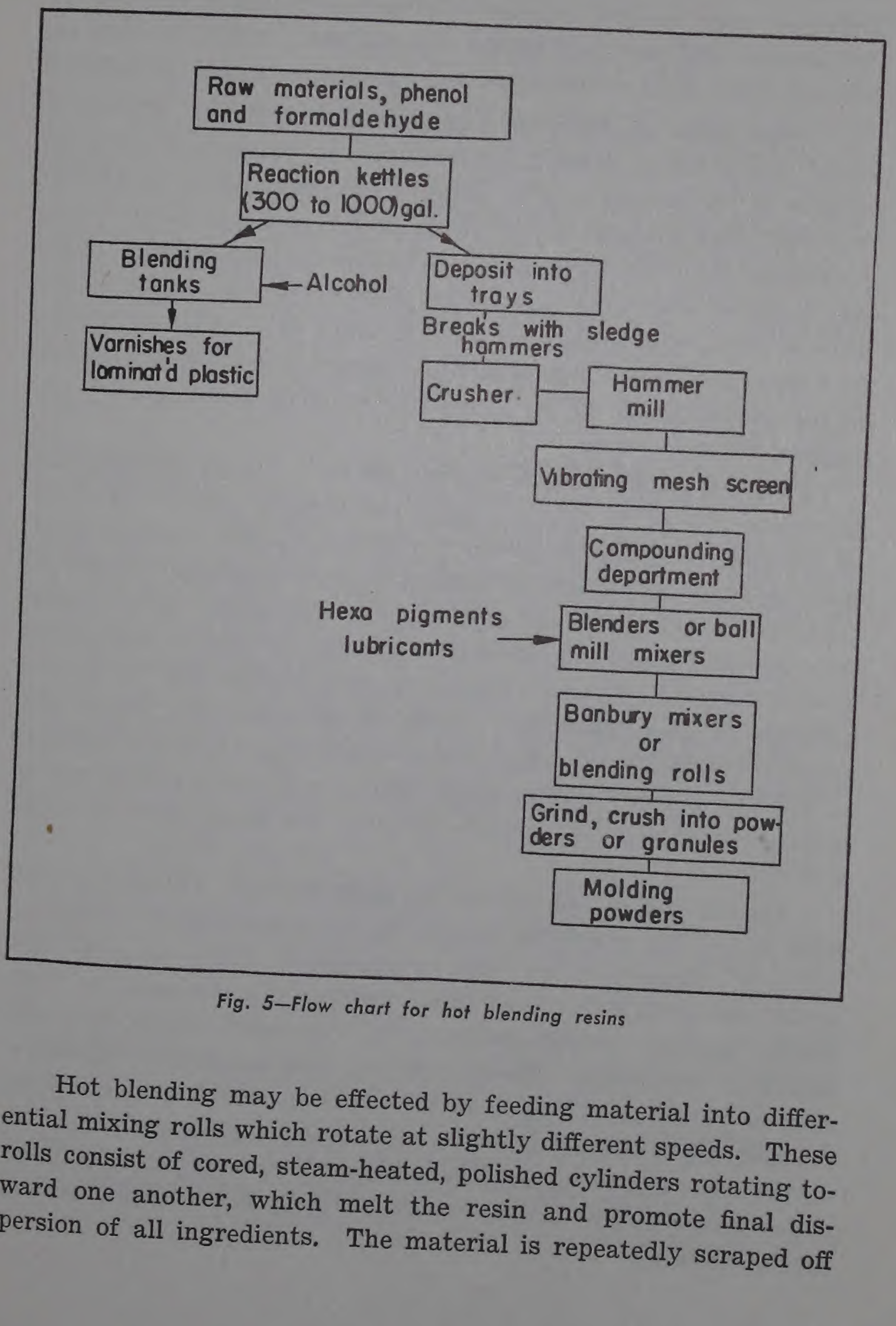


Fig. 5—Flow chart for hot blending resins

Hot blending may be effected by feeding material into differential mixing rolls which rotate at slightly different speeds. These rolls consist of cored, steam-heated, polished cylinders rotating toward one another, which melt the resin and promote final dispersion of all ingredients. The material is repeatedly scraped off

the rolls by doctor blades and thrown back for thorough remixing and rubbing of particles. In some plants this operation is fully automatic, as the time element is quite important. Hot blending is also performed in internal mixers of the Banbury type, as illustrated later in this chapter. After hot blending the batches are ground and screened to the desired size. Many batches are blended together to insure uniformity of product as sold to molders.

Preparation of Phenolic Laminating Varnishes: Phenol or cresol resins for laminating generally are prepared by a one-stage process in the presence of an alkaline catalyst such as ammonium hydroxide and a slight molar excess of formaldehyde. After substantially all of the formaldehyde has reacted and after the aqueous layer of water has been removed, the resin is cut by a suitable solvent such as alcohol or a mixture of 9 parts of alcohol to 1 part of toluene. Approximately 50 per cent solids are present in the final varnish, which is used for treating cloths, papers, and various sheet products.

Preparation of Phenolic Casting Resins: Liquid casting resins generally are of a lighter color, and greater care is exercised in utilizing pure materials which will not discolor the final product. A large molar excess of formaldehyde-to-phenol (about 2.5 to 1) is reacted under strongly alkaline conditions. After a suitable reaction period, the resin is made slightly acid by adjustment with lactic acid. This is followed by dehydration and the further addition of pure glycerine. These liquid resins are poured and cured immediately in a high-temperature oven after the inclusion of suitable glycerol-soluble dyes. Other varieties are stabilized to prolong their shelf life and, before use, are mixed with catalysts and fillers.

Preparation of Oil-Soluble Phenolic Resins: Oil-soluble phenolic resins are employed largely in the manufacture of surface coatings. Natural resins, rosin in particular, confer upon the phenolics the property of combining with drying oils such as tung, perilla, linseed, or dehydrated castor oil, with which they are otherwise immiscible. Special 100 per cent substituted phenolics, such as para-phenyl phenol or p-tert.-amyl phenol, are capable of reacting with formaldehyde to form resins which are soluble in drying oils without further modification. Films formed from these resins generally are baked, drying by processes of oxidation and polymerization.

Special Types of Phenolic Resins

A few special types of phenolic resins are herewith reviewed. They resemble phenolics in end use and appearance, but sometimes are identified by other names:

Phenol-Furfural Resins: As already noted, these resins are formed when furfural replaces formaldehyde, and molding compositions, laminating varnishes, and adhesives from these materials are well known. While they may exhibit increased fluidity during molding, slightly longer cure times generally are required. Furfural also functions as a highly active wetting agent, making possible the efficient distribution of phenol-formaldehyde binders in the manufacture of grinding wheels. There is only one major manufacturer of phenol-furfural compositions, and at least eight major manufacturers of phenol-formaldehyde resins.

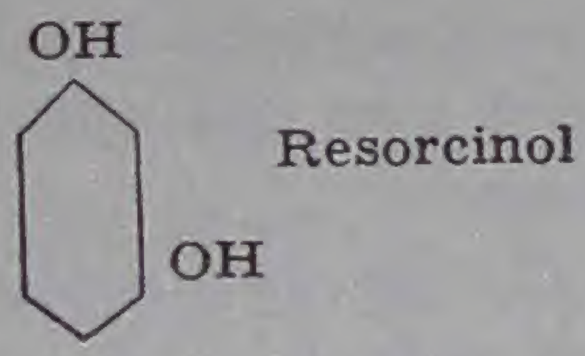
Phenol-Formaldehyde-Hardwood Pitch: The Second World War brought forth several important molding compositions which required less of the critical phenol-formaldehyde resins than the conventional types. One of these employed hardwood pitch, with a good deal of success, to fulfill many important applications. Among other prominent extenders for the phenolics, particularly in laminating varnishes, was "vinsol", a gasoline-insoluble fraction of pine-tree residuum.

Phenolic Resin—Lignin Enriched: The majority of the useful lignin molding compounds have incorporated therein a small amount of phenol-formaldehyde resin. While there is a considerable saving in the amount of phenolic resin required for ordinary wood-flour (as much as 50 per cent is saved), the appearance, good flow during molding, and ease of removal from the hot mold are dependent upon the presence of the phenolic resin binder.

Soya-bean Plastics, Cottonseed-hull Plastics, Bagasse Plastics: A number of the special molding compounds prepared from waste vegetable products are dependent upon the presence of a small amount of phenol-formaldehyde resin. In some cases the fillers are treated with formaldehyde, to improve the flow qualities and reduce the amount of the more expensive synthetic resin required. However, molding and physical properties are much dependent upon the presence of the phenolic constituents.

Resorcinol-formaldehyde: Still a relative newcomer to the phenolic plastics picture, though a very important one, is resorcinol.

The structure of resorcinol is shown herewith:



Resorcinol

It has been known for a long time that resorcinol has excellent resin forming properties, though commercial interest was curtailed because of its very high price. Since 1941, however, the price of technical resorcinol was lowered to 58 cents per pound (phenol costs 9-10 cents per pound) and a number of specialty adhesives made their appearance. These are prepared with a molar excess of resorcinol over formaldehyde, though the deficiency is made up at the time of application, when paraformaldehyde is added. These adhesives feature low-temperature setting, and cure under mildly alkaline conditions (pH 7.0 to 7.5).

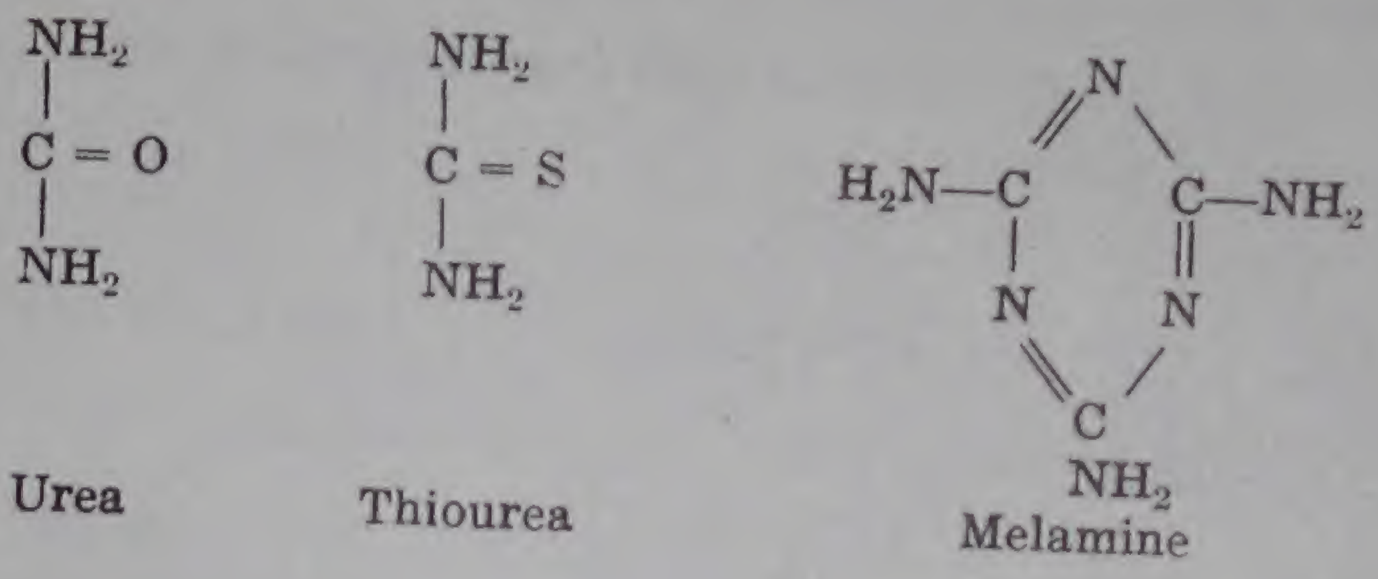
Phenolic Resins-Synthetic Rubbers: Within recent years considerable research has been in progress on combinations of certain of the phenolic resins with synthetic rubbers. Some of the combinations have found important outlets as rubber and metal adhesives, while others show promise in the field of molding materials. In particular, butadiene-acrylonitrile synthetic rubbers (for example, "Hycar-OR") and phenolics have been united to develop molded parts of very high impact strength. The chemical nature of this association is not fully understood, though there is some evidence that a partial phenolic resin polymer may serve as a vulcanizing agent. When the rubber is the major component, the phenolic resin additions increase stiffness and tensile strength.

Urea and Melamine Formaldehyde Resins

Urea and melamine formaldehyde plastics constitute the other major group of moldable thermosetting plastics. While higher in price than the phenolics, they nevertheless possess outstanding advantages in color selection and desirable electrical properties.

Urea and melamine or combinations of both, and sometimes to a lesser degree, thiourea, are reacted with formaldehyde to form a number of useful resins. The structure of each of these three materials is shown herewith, each in appearance being a white

water soluble crystalline material:



Urea Thiourea Melamine

In determining the reactive points upon these reagents, the hydrogen atoms of the NH_2 groups generally are considered capable of reacting with the oxygen of formaldehyde to form water, in a typical condensation-polymerization reaction. The products of the reaction are very much dependent upon the pH, the relative proportion of formaldehyde to urea, prevailing temperature, and time of reaction. Under mildly alkaline conditions (pH 7.5 to 8.0), the

TABLE IV

Urea and Melamine Formaldehyde Resins

Raw Materials

Ammonia, carbon dioxide, wood alcohol

Reagents

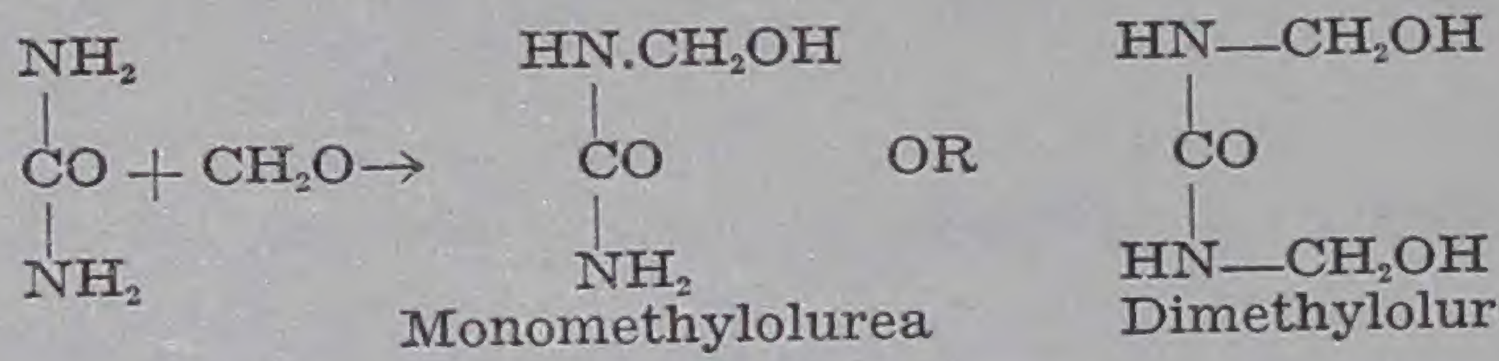
Urea crystals, melamine, formaldehyde

Products	Typical Applications and Trade Names
MEDIUM-MOLECULAR-WEIGHT RESINS (heat-convertible types)	
Solid, fusible types compounded with catalysts, pigments, lubricants, and fillers (usually alpha-cellulose)	Molding compounds ("Plaskon", "Beetle", "Melmac")
Water-soluble powders.	Laminating varnishes
Resins prepared in presence of butyl alcohol	Surface coatings
Resin solutions or powders plus catalysts.	Adhesives and impregnants ("Uformite", "Weldwood", "Melurac", "Resloom")
HIGH-MOLECULAR-WEIGHT RESINS (polymerized materials)	
Decorative laminated sheets	
Molded articles	

formation of monomethylolurea or dimethylolurea is favored. Which one, however, depends upon the proportion of formaldehyde. Dimethylolurea (D.M.U.) may be recognized as a white crystalline compound which is sold commercially and recommended for combining in aqueous solutions with urea crystals for treating wood products. After a suitable period of impregnation and diffusion,

the resin may be cured with heat and improve the appearance, hardness, and water resistance of the wood.

The reaction between urea and formaldehyde may be depicted in the following manner:



When conducted under mildly acidic conditions (pH 5.0 to 6.0) as it is done in some commercial processes, low temperatures are necessary to avoid too rapid an approach to the infusible, insoluble stage. Under the conditions of mild acid catalysts, the formation of dimethyleneureas is favored, proceeding to the more advanced stage of polymerization. The final, infusible, insoluble stage "C" form of urea-formaldehyde resin is open to some question, though latest evidence points to a methylene bis-amide (CO-NH-CH_2-NH-CO) linkage between cyclic trimethylenetriamine compounds. The urea is surmised to react as an amino acid amide.

Urea formaldehyde polymers are less stable to heat and water than phenolics, though with the advent of melamine-formaldehyde resins, a considerable improvement was effected. While a solid block of urea-formaldehyde resin may be prepared it will be found to shrink and check very badly unless the proper fillers have been added. Nevertheless it is well known that the after or service shrinkage of urea resins is appreciably greater than that of the phenolics. Alternate exposures of high and low humidities will tend to play havoc with urea resin moldings, though this has been corrected to a large measure by the more water-resistant melamine resins.

Preparation of Urea Resin Molding Compounds: An infinite variety of color possibilities feature the urea and melamine formaldehyde molding compounds. Light, translucent pastel shades are available in various colors to any degree of opacity. As may be expected considerable care is exercised in the manufacture and the application of molding powders to avoid contamination with dirt or dust, which may mar an otherwise attractive piece. Monel metal, nickel-clad or chromium-plated kettles and processing equip-

ments are necessary. In the selection of fillers, pure alpha-cellulose sheets are specified, inasmuch as when they are impregnated and cured, they permit a high degree of translucency.

In the manufacture of the resin, generally a molar excess of formaldehyde to urea is practiced (1.5 to 1.8 mols to 1). After initial reaction, which may be for several hours at about 30 C, the resin is passed through a special filter to remove dirt and impurities. Drying at a low temperature is essential to avoid setting-up the resin prematurely. The shredded alpha cellulose may be introduced into the resin solution in a wet mixing operation, and before drying commences. From 30-40 per cent alpha cellulose is added (based on total weight).

After drying, the material emerges from the oven looking much like pop-corn. This is broken up and stored in sealed containers until ready for further processing. The flow chart in *Fig.* 6 outlines one typical commercial procedure. The urea-formaldehyde condensate and filler are now ground up in a ball mill, using porcelain balls. During this operation final adjustments are made on the flow properties of the material by adding free urea or paraformaldehyde and catalysts, and the necessary lubricants and coloring agents introduced. Samples are withdrawn frequently for molding tests and color comparisons. The finely divided powder must now be converted to a more granular condition for ease in handling during the molding, and a hot blending followed by grinding and screening prepares the final compound.

Urea and melamine molding compounds have been specified for large moldings such as housings for weighing scales or deep translucent bowls for lighting fixtures, and it has been necessary to develop long flowing qualities in the material which would permit the attainment of compound shapes. To permit satisfactory and economical molding of a wide assortment of engineering designs, the materials manufacturers are offering several urea molding compositions with various degrees of plasticity. Hard types are suited to fast curing cycles for buttons, buckles, and small knobs, while soft types are suited to large housings.

While the great majority of urea and melamine-formaldehyde molding compounds have employed alpha cellulose as a filler, there are special mineral-filled grades which feature high temperature resistance and good dielectrical properties. Only the urea and melamine molded ignition distributor housings have possessed

sufficient arc resistance to satisfy the requirements of high-altitude aircraft.

Most urea and melamine compounds are prepared with small amounts of latent catalysts which are activated by heat or moisture. It is essential that the molding materials be stored in a dry

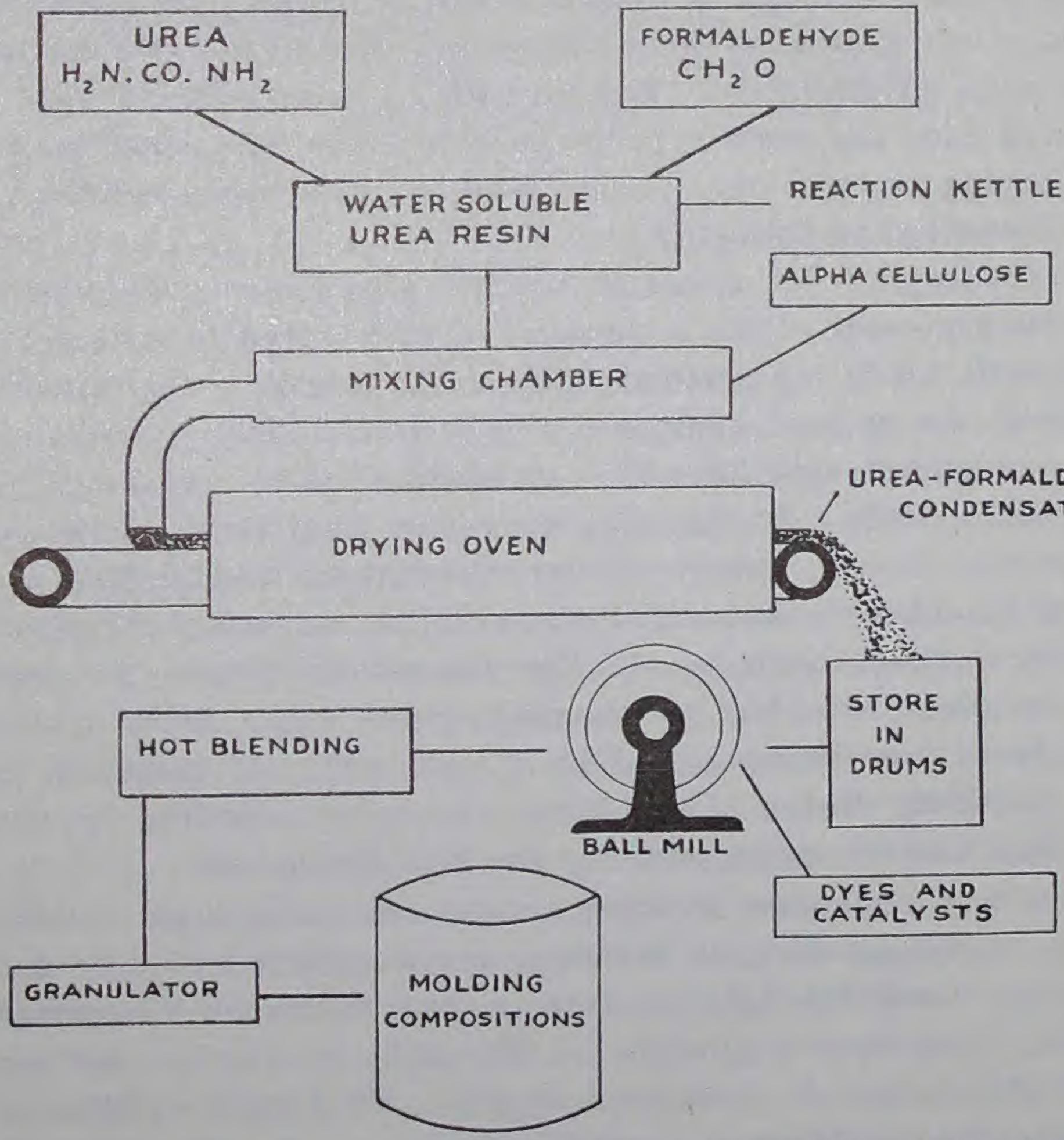


Fig. 6—Flow chart for preparation of urea molding compounds

and cool place by the molder if they are to be kept for any length of time. A drum of material should not be left open any longer than necessary and should not be exposed promiscuously to the atmosphere. Failure to observe care in handling and storage will result in deterioration and loss of good molding characteristics.

Preparation of Urea and Melamine Resin Adhesives: Urea and melamine resin adhesives have been particularly adaptable to the

cementing of wood, paper, and miscellaneous cellulosic products. They generally are prepared in a ready-prepared dry mix which requires only the addition of water for activation. The water generally activates catalysts, which usually are ammonium salts of strong acids. These adhesives possess considerably better water resistance than their prototypes among the proteins, animal, or vegetable adhesives.

Preparation of Urea and Melamine Resin Impregnants: Aqueous solutions of urea and melamine-formaldehyde resins have been widely adapted to the impregnation of paper and textile products. Two or three per cent resin in paper for example, has been sufficient to give it a high wet strength, without affecting its softness or absorbing qualities. In the development of crease-resistant fabrics and in the transformation of natural fibers to high quality, improved materials, these colorless resins have been invaluable both as impregnants and coatings.

Preparation of Urea and Melamine Resin Coatings: Coatings of urea or melamine-formaldehyde resins would tend to check severely in the course of time if aqueous solutions were applied to nonporous surfaces. A modified form of the resin has been developed, however, which is playing an outstanding role in the field of baked enamels. In particular the formation of a urea-formaldehyde-butyl alcohol resin has proved invaluable, particularly in combinations with alkyds. This same combination is true for melamine-formaldehyde-butyl alcohol reactions. The baked enamels will withstand very high temperatures without much loss of gloss and color.

Alkyd Resins

The products derived from alkyd resins are largely found in the surface coating industry. As was noted in the first chapter, they rank with phenolics in total resins produced. In their applied state they appear in a modified form, generally to promote compatibility with various drying oils.

While alkyd (coined from alkyl and acid) resins have been developed for a number of years and their major applications have appeared largely in surface coatings, they represent a potent source of new materials, which may well have a major influence in other fields. The reaction of glycerol with phthalic anhydride for example, is illustrated herewith in formation of an ester,

TABLE V

Alkyd Resins

Raw Materials

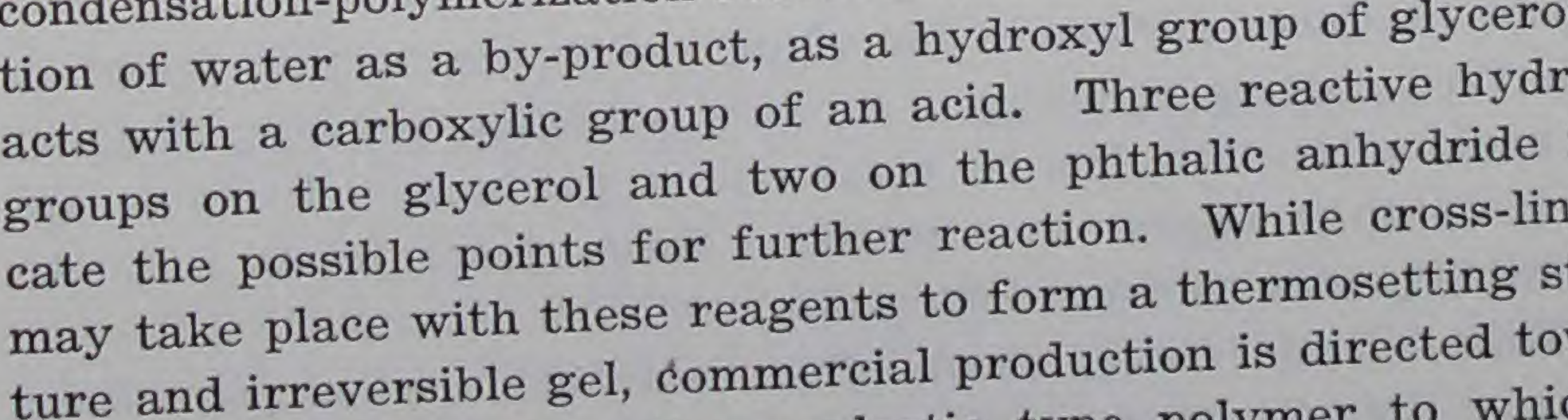
Animal fats and greases, ethyl alcohol, methyl alcohol, ethylene	Coal tar (naphthalene), benzene, rosin (pine tree), drying oils

Reagents

Glycerol, pentaerythritol, glycols	Phthalic acid, maleic acid, rosin (abietic acid), fatty acids

Products	Typical Applications and Trade Names
MEDIUM-MOLECULAR-WEIGHT RESINS	
Oleoresinous varnishes (blended with various oils)—heat convertible	Surface coatings ("Glyptal", "Beckacite", "Rezyl")
Resin solutions	Adhesives and coatings
HIGH-MOLECULAR-WEIGHT RESINS (polymerized materials)	
Certain synthetic rubber-like materials	"Paracon"

phthalic-acid monoglyceride, a typical reaction product of polybasic acid and a polyhydric alcohol:

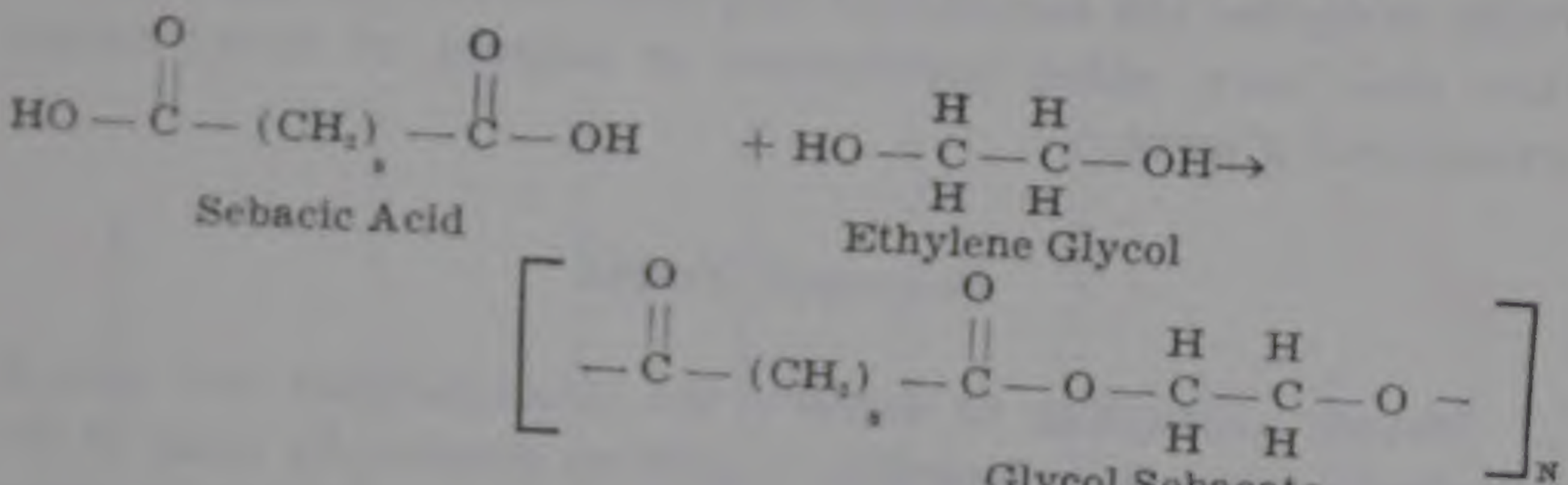


Phthalic Anhydride Glycerol Phthalic-Acid Monoglyceride

In visualizing the growth of the polymer from this ester, the condensation-polymerization reaction is anticipated with the formation of water as a by-product, as a hydroxyl group of glycerol reacts with a carboxylic group of an acid. Three reactive hydroxyl groups on the glycerol and two on the phthalic anhydride indicate the possible points for further reaction. While cross-linking may take place with these reagents to form a thermosetting structure and irreversible gel, commercial production is directed toward producing a long-chain thermoplastic type polymer to which is chemically combined an unsaturated fatty acid such as linoleic acid which is also capable of cross-linking.

A new realm of plastics chemistry is opened with maleic anhydride, which is capable of chemically combining with certain con-

jugated unsaturated materials to form what are called "adducts". These "adducts", in turn, react with polyhydric alcohols to form new types of alkyd resins. Two commercially important reagents are prepared from dipentene and cyclopentadiene with maleic anhydride. For a long period of time glycerol was the sole polyhydric alcohol of major importance in the preparation of alkyd resins, though pentaerythritol and polypentaerythritol, prepared from acetaldehyde and formaldehyde, are growing in importance. More work has been accomplished in recent years to produce rubber-like elastomers from the alkyd resins through the reaction of dibasic acids such as sebacic acid or succinic acid with the dihydric glycols. One of these is illustrated herewith ("Paracon"):



Sebacic Acid

Ethylene Glycol

Glycol Sebacate

Thermosetting type alkyd resins are modified with drying or non-drying oils, or the fatty acids of these oils; with natural resins and synthetic resins from phenolic or urea resin groups to comprise the formulation of various oleoresinous varnishes. (These compositions are evaluated more fully in the chapter on surface coatings). As molding materials, the utilization of alkyd resins is limited, largely because the time required to convert to a hard, rigid, infusible, insoluble state is much longer than for equivalent phenolic or urea materials. As binders, they have been employed, however, in the manufacture of sheets of mica splints, used extensively by electrical appliance manufacturers.

Polyesters: Related chemically to the alkyd resins, various polyesters or unsaturated alkyds have made their appearance within the past few years. The products have been largely employed as casting or laminating resins, and form the basis of many of the so-called low pressure laminates, so widely employed in the production of large contoured sections, as in small boats and aircraft semistructural parts. These liquid or paste-like heat convertible resins are activated by catalysts, such as lauryl or benzoyl peroxide,

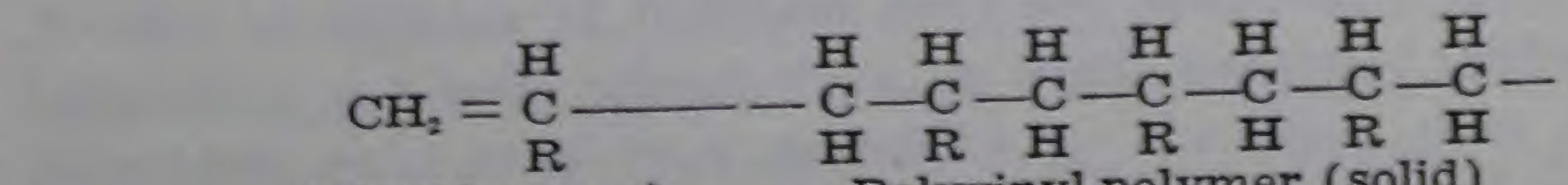
or t-butyl hydroperoxide and cured with heat and low pressures upon relatively low cost tools, as compared to the high-pressure molding operations.

Polyester resins are prepared on one hand with unsaturated or saturated polycarboxylic acids, unsaturated monocarboxylic acid, or their chlorinated derivatives, and on the other hand with unsaturated alcohols or hydroxy substituted acids. Prominent among the unsaturated alcohols is allyl alcohol, while among the acids, diglycollic acid, maleic anhydride, or phthalic acid are representative. Hard, brittle, infusible, insoluble polymers are formed, and to render them more tough and less brittle, sometimes a thermoplastic partial polymer of styrene or vinyl acetate are included. These comprise the commercial polyester resins. To the engineer they also have added significance as sources of heat-resistant transparent glasses.

Polyvinyl Resins

Before attempting to describe the characteristics and uses of polyvinyl resins, it is desirable to present graphically some of the many types of polyvinyl resins and their inter-relationships. These are described more fully in *Fig.* 7.

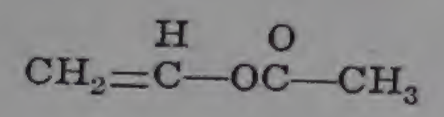
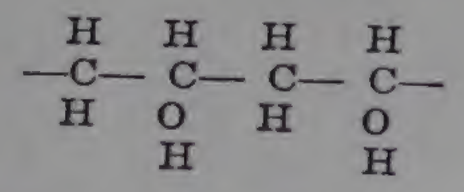
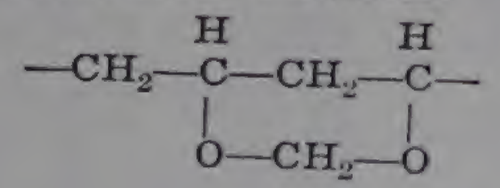
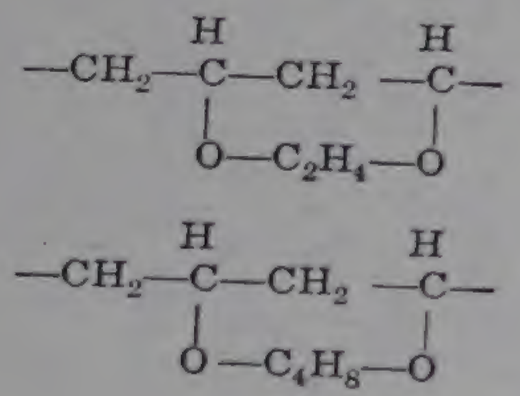
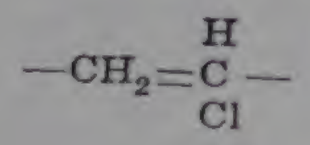
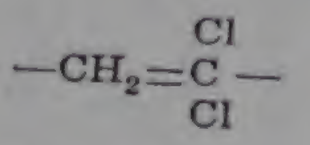
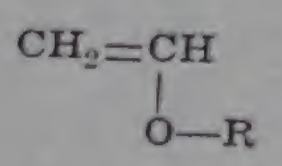
The vinyl grouping has become well known in the field of synthetic resins, as a number of useful materials have been developed from this structure. The general mechanism of the chain-wise polymerization may be indicated in the following manner:



(Liquid or gas) Polyvinyl polymer (solid)

The monomers of the vinyl resin groupings also lend themselves to copolymerization with other vinyls or other polymerizable monomers. Styrene, for example, also may be copolymerized, as well as methacrylic acid esters to achieve a wide variation in properties. Many of the vinyls are polymerized in solution, with the aid of heat and catalysts. Close control is exercised over the polymerization, as the average molecular weight of the polymers determines the physical and chemical characteristics. A short de-

FIG. 7
Types of Vinyl Resins

Name		Preparation	Typical Applications and Trade Names
VINYL ACETATE		Acetylene—acetic acid	Adhesives, manufacture of polyvinyl acetals, emulsions (''Vinyseal'', ''Gelva'')
POLYVINYL ALCOHOL		Hydrolysis of polyvinyl acetate or formate	Extruded tubings, water-soluble powders (''PVA'', ''Resistoflex'')
ALDEHYDE MODIFIED POLYVINYL ALCOHOLS			
Polyvinyl Formal		Reaction of formaldehyde on polyvinyl alcohol	Wood adhesive, wire insulation, molding compounds (''Formvar'')
Polyvinyl Acetal		Reaction of acetaldehyde on polyvinyl alcohol	Nonmetallic hammer heads
Polyvinyl Butyral		Reaction of butyraldehyde on polyvinyl alcohol	Safety glass interlayer, waterproofing textiles, shoe soles (''Butacite'', ''Butvar'')
VINYL CHLORIDE		Acetylene-hydrochloric acid, by-product in ethylene glycol manufacture	Chemically resistant coatings. Highly plasticized varieties—(''Flamenol'', ''Korogel'', ''Koroseal'', ''Tygon'')
VINYLIDENE CHLORIDE		Trichloroethane-lime	Useful copolymers with vinyl chloride
Vinyl Ethers		Acetylene and alcohols (R-OH)	Coatings and adhesives
Copolymers			
Vinyl Chloride-	Vinyl Acetate	87:13, 90:10 proportions typical	Rigid, nonrigid sheets and extrusions, coatings (''Vinylite'', ''Vinyon'')
Vinyl Chloride-	Vinylidene Chloride	90:10 for some and 10:90 for others	Molding compounds, textiles, extrusions (''Saran'', ''Geon'')

scription of each of the more important polyvinyl resins follows:

VINYL ACETATE: Clear vinyl acetate, a thin liquid boiling at 73 C, is an important constituent in the manufacture of aldehyde modified polyvinyl alcohols. As a polymer it is available in different degrees of molecular weight and softening points. It generally is sold as a solution adhesive for miscellaneous uses, though interest has been displayed in a high-solids-content (55 per cent) emulsion which has much lower viscosity than solutions of lower solids contents. As an adhesive, highest strengths are realized in hot melt applications. The polyvinyl acetate is readily compatible with numerous chemicals and modifiers.

VINYL CHLORIDE: A gas in monomer form, vinyl chloride may be polymerized in solution to a number of chemically resistant compositions. Its major uses are in the manufacture of numerous copolymers. Polyvinyl chloride is quite resistant to solvents and strong acids or alkalies. In a pure state it has a high melting point, though when properly compounded with appropriate plasticizers it may be reduced to a useful rubber-like consistency, resistant to greases and oils and stable to oxidation effects which embrittle rubber. Rubber-like formulation of polyvinyl chloride and polyvinyl chloride-acetate copolymers have found extensive use on shipboard and aircraft as electrical insulation and non-rigid members or coatings.

Polyvinyl chloride and its copolymers, including acrylonitrile and polyvinylidene chloride, are widely employed now as thin transparent packaging foils, extruded tubings of all sizes, textile and paper coatings, and electrical insulation. New and significant applications are developing quite rapidly for this group of versatile plastics. In the field of plaster patterns and casts, the pattern shops are gradually changing from glue to rubber-like molds of plasticized polyvinyl resins. Further developments such as "Geon Polyblend" where combinations with synthetic rubbers are effected, will increase the scope of these materials.

The paste-like resins prepared from polyvinyl chloride copolymers have attracted much attention. Chemically they are a suspension of 50-60 per cent finely powdered resin in a plasticizer. This paste-like fluid is quite stable until it is heated to a high temperature (usually in the vicinity of 300 F.), at which point it converts to a rubber-like gel. Interest focuses on castings and coatings of the vinyl paste resins, as well as foamed structures.

POLYVINYL CHLORIDE-ACETATE: The copolymerization of polyvinyl chloride-acetate generally is carried out in a solution of acetone and the copolymer precipitated with water after the reaction is completed. The copolymer appears as a fine powder, which then is washed and dried for further compounding. The properties of the polyvinyl copolymer as a function of molecular weight and proportion of ingredients are expressed in the following table, prepared from data by Dr. Bonnet (A.A. Textile Chemists—Jan. 25, 1940):

Properties of Polyvinyl Chloride-Acetate

Per Cent Vinyl Chloride	Molecular Weight	Applications
65—70	4000— 6000	Coatings—compatible with nitrocellulose
86—87	8500— 9500	Tough films, good solubility
86—87	9500—10500	Paper coatings, floor tile, phonograph records
85—88	12000—13000	Molding compositions
88—90	15000—16000	Sheet stock—tough

The greater the proportion of the vinyl chloride component, the better the chemical resistance and the greater the difficulty in dissolving the material. Numerous rigid and non-rigid (rubber-like) grades of this copolymer are commercially available. In processing the material, when producing blends of plasticizers, pigments and lubricants, equipment of corrosion-resisting nonferrous metals, or chromium plated metals are preferred. Polyvinyl chloride is unstable at temperatures above 300 F when in contact with steel or zinc, and in molding or extruding the material or its copolymers, special heating or plasticizing chambers are desirable. Low-temperature flexibility is a highly desirable quality in the rubber-like varieties, and recent developments in plasticizers such as dioctyl or trioctyl phosphate (Clash-Berg. *Modern Plastics* Vol. 21, page 119, July, 1944) have made this possible. Polyvinyl chloride-acetate generally is compounded with stabilizing agents of lead, cadmium, or alkaline earth soaps.

POLYVINYL ALCOHOL: The chemical resistance of polyvinyl alcohol is outstanding, making possible numerous uses to chemical processing equipments handling organic chemicals and solvents. The solubility is dependent upon the degree to which the polyvinyl acetate was hydrolyzed to polyvinyl alcohol. In commercial forms extruded tubings and sheets are well known, generally being plasticized with a substantial amount of glycerine and a small amount

of formamide. There are commercial grades of polyvinyl alcohol which will dissolve in water. In the design of special valves, O-rings of polyvinyl alcohol have proved invaluable in resistance to aromatic fuels used on aircraft.

ALDEHYDE MODIFIED POLYVINYL ALCOHOL RESINS: Comprising an entire family of resins by themselves, the aldehyde modified polyvinyl alcohols have featured toughness and rubber-like qualities when properly plasticized. In developing the properties of the final polymers, there are three components to consider: Polyvinyl acetate, polyvinyl alcohol and the aldehyde modified resin. By properly balancing one component against another a wide degree of solubility or hardness may be attained. In addition, thermosetting qualities may be imparted through chemical combination with phenol-formaldehyde partially polymerized resins, which like most polyvinyl acetals are soluble in alcohol.

As a tough rubber-like film, plasticized polyvinyl butyral has found extensive application in the manufacture of automobile safety glass, though at the start of the Second World War this market disappeared and was superseded by coatings on textiles to improve water resistance. When high altitude bombers required more shock-resistant transparent enclosures than were available from acrylics alone, laminates were prepared using polymethyl methacrylate faces and polyvinyl butyral interlayers measuring 3/16-inch in thickness. Tough, abrasion-resistant magnet-wire coatings of polyvinyl formal now are extensively employed. A knot may be tied in a small gage wire without cracking the insulation. A considerable production is now in progress employing polyvinyl acetals in nonmetallic hammer heads.

POLYVINYLIDENE CHLORIDE: Copolymers employing polyvinylidene chloride as a major component, such as Saran, exhibit excellent chemical resistance, and hence find important applications on chemical processing equipment. Because its high chemical resistance precludes the use of solvents (there are no known effective solvents for Saran), coatings are applied from a latex dispersion. Films of this resin offer high resistance to water and vapor permeation. The protection of machine parts by Saran film was carried out during the war.

Molded and extruded parts of polyvinylidene chloride exhibit a marked degree of crystallinity. Cold stretching of filaments will develop tensile strengths of 50,000 psi. To develop high-

strength pieces, Saran is injection molded into a warm die in the vicinity of 190 F, at which temperature re-crystallization will occur rapidly. When molded into dies at room temperature, soft, flexible, amorphous pieces are obtained. Woven screens of polyvinylidene chloride and extruded sections for upholstery material are well known.

Acrylic Resins

The polymeric esters of acrylic acid and methacrylic acid are well known for their many useful properties. In particular, polymethyl methacrylate has come to be recognized for its outstanding clarity and good weather resistance. During the war, its entire production went largely into the manufacture of transparent enclosures for aircraft, though normal peacetime pursuits include numerous machine models and decorative, fabricated objects.

Acrylic Resins

Raw Materials—Petroleum, nitrogen (air) and alcohols
Reagents—Ethylene, hydrogen cyanide, sodium cyanide, alcohols, sulphuric acid, acetone
Products—Polymerized sheets, rods, and tubes, molding compounds
Tradenames—"Lucite" and "Plexiglas"

In the commercial preparation of acrylic acid and its derivatives, ethylene is reacted with hypochlorous acid to produce ethylene chlorhydrin. This is condensed with sodium cyanide to form ethylene cyanohydrin which, if dehydrated, forms acrylonitrile, a highly useful resin which copolymerizes with butadiene to form an important synthetic rubber. Simultaneous dehydration and esterification in the presence of an alcohol and sulphuric acid leads to the formation of an acrylic ester:

$$CH_2OH.CH_2Cl + NaCN \rightarrow CH_2OH.CH_2CN + NaCl$$

Ethylene Chlorhydrin

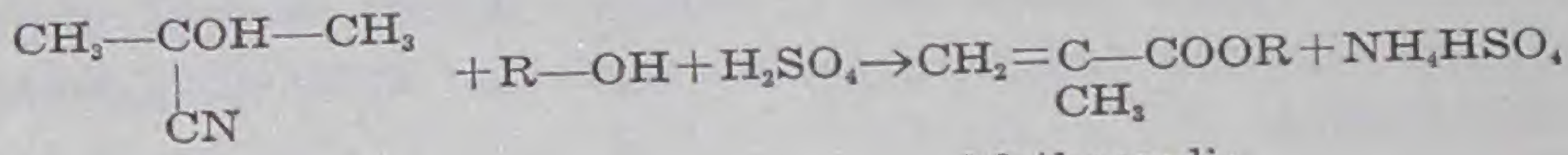
$$CH_2OH.CH_2CN + R-OH + H_2SO_4 \rightarrow CH_2=CH-COO-R + NH_4HSO_4$$

Acrylic Ester

When R in the preceding equations is CH_3, as in methyl alcohol, the acrylic ester is methyl acrylate, with the formula

$$CH_2 = CH - COO - CH_3.$$

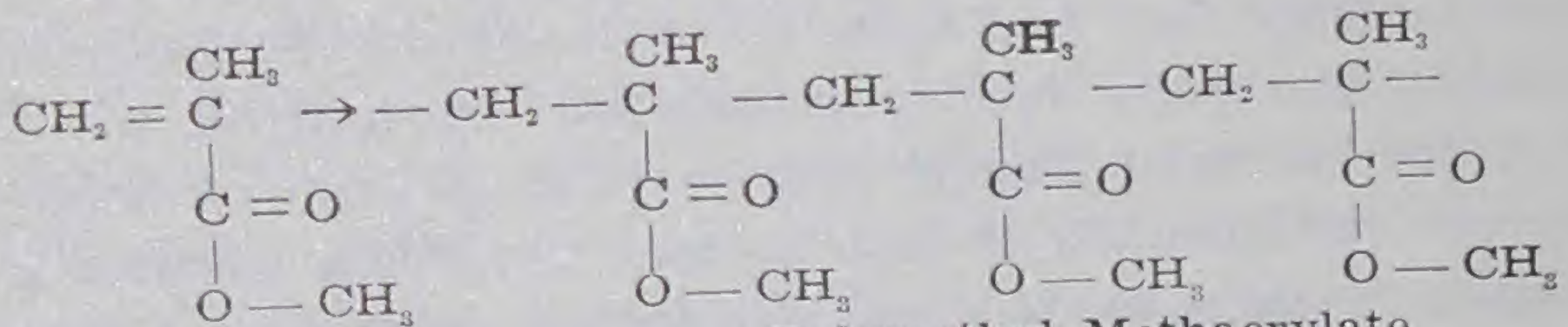
Esters of methacrylic acid may be prepared by reacting acetone cyanohydrin with an acid and the desired alcohol:



Acetone Cyanohydrin

Methacrylic Ester

When R in the above equation is CH_3, as in methyl alcohol, the methacrylic acid ester is methyl methacrylate:



Polymethyl Methacrylate

In a similar manner, higher homolgues may be prepared. Another interesting member is butyl methacrylate, of lower softening point in the polymeric form, and proposed as a hot melt composition. As in the case of the vinyl resins, the acrylic and methacrylic acid esters may be copolymerized to achieve a wide diversification of properties and much of the future of these materials lies in this direction. Copolymers of styrene and methyl methacrylate have already been used commercially as hard, transparent materials. Ethyl acrylate has also been present in some compositions. In general, the polymethacrylates are harder than the corresponding polyacrylates, though the greater the length of the substituent forming the side chain, the softer the material and lower the tensile strength.

The polymerization of methacrylate esters is a highly exothermic one, the heat of reaction being approximately 80 calories per gram. Under carefully controlled conditions with respect to rate of reaction, a direct thermal polymerization of methyl methacrylate may be carried out in standard molds for tubes and bars. The temperature of polymerization is very important for methacrylate esters and, when polymerization is conducted on a solid mass of material, seldom exceeds 125 to 130 F. In fact, when casting liquid monomers into solid form in a constant-temperature oven, it is sometimes preferred to cast in layers to avoid formation of

bubbles on the inside of the casting. Other techniques have been developed in which a definite temperature gradient is applied to the mold, with the highest temperature at the bottom of the vessel slowly moved up over a period of several days.

Molding Compositions: Instead of grinding down a large mass of material into powdered form suited for blending into molding compositions, a more satisfactory technique known as emulsion polymerization is preferred for preparation of granules of the polymer. An aqueous emulsion of the monomer is prepared which, in conjunction with a dispersing agent and vigorous stirring, yields the polymer in powdered form. By controlling temperature, rate of addition of monomer, and other factors, the size of the polymer may be controlled.

Further compounding of polymethyl methacrylate molding compositions may be accomplished in a Banbury mixer. There, various dyes and pigments may be added together with lubricants and small amounts of monomer to improve flow properties, as well as catalysts such as benzoyl peroxide. Oxygen-bearing catalysts are most effective in promoting the polymerization of acrylics.

It is significant that injection molding compositions of acrylics do not necessarily require plasticizers as do other thermoplastics such as cellulose plastics. While plasticizers improve flow during molding, they also introduce their own limitations into the composition.

Recent developments in acrylic resins have tended toward compounds with improved temperature resistance, and some molded parts will exhibit ASTM heat distortion points near 200 F. Transparent acrylics have served many useful functions as molded and fabricated parts as, for example, illustrated in *Fig.* 8, where the circulating fluid may be inspected. Special optical goods and large television magnifying lenses find these transparent plastics most useful.

Sheets and Tubes: One of the most popular materials from the standpoint of fabrication operations such as machining, drawing, forming, and blowing, is the standard sheet and tube stock of polymethyl methacrylate. Available in thicknesses from 1/16-inch up, sheets of acrylic plastics have found their way into a wide variety of industrial and decorative articles. By fabricating complicated machine parts of clear acrylic plastics, it has been

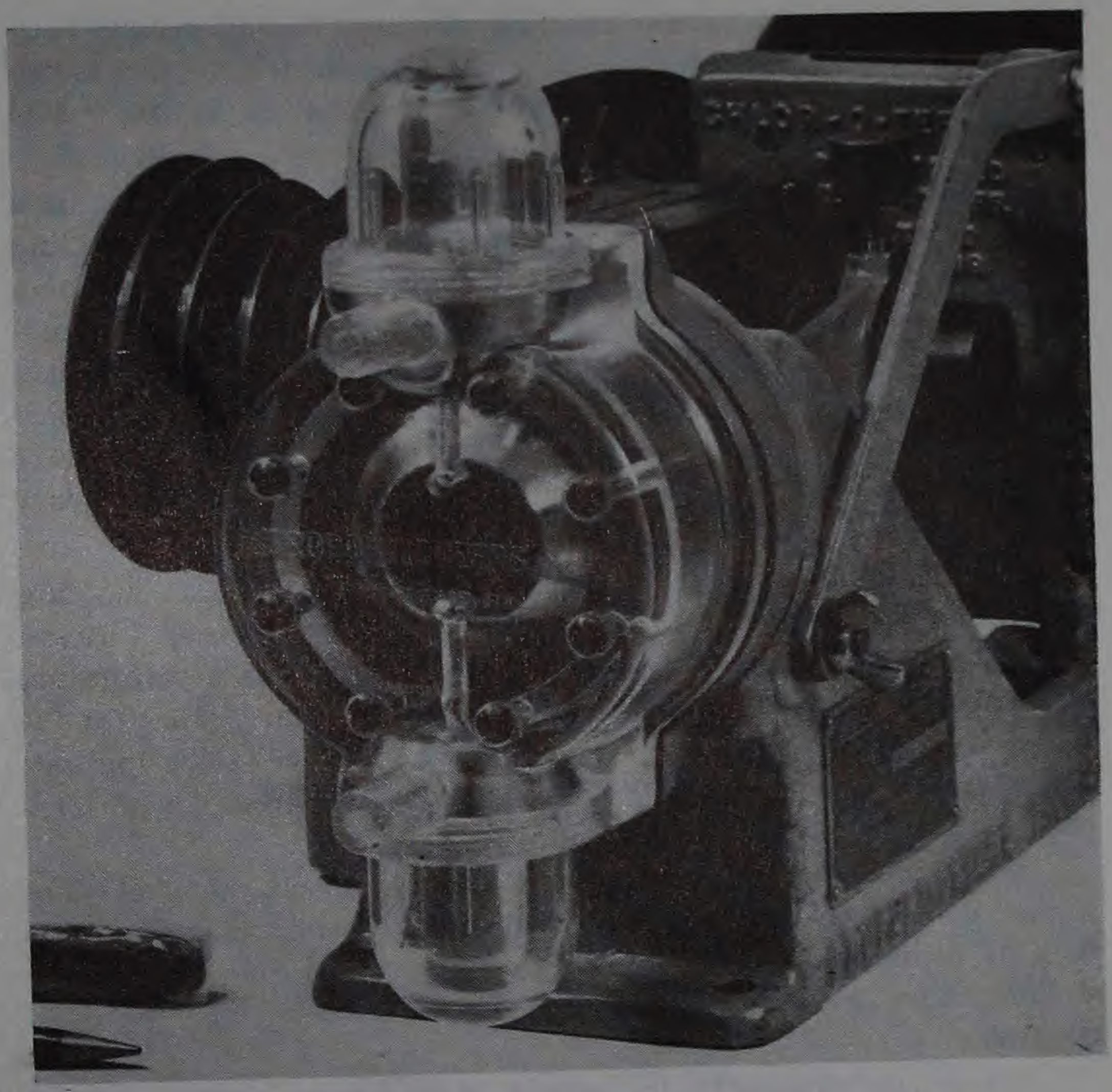


Fig. 8—Molded transparent enclosure permits visual inspection

possible to study important machine operations, and make improvements in design efficiency.

Some of the sheet stock is prepared by molding of fine granules rather than by casting of liquid resins. These sheets are quite clear and well suited to many purposes, though not as strong as the cast sheets. Fabricators of the sheet stock report better results with cast sheets, though economic reasons often require use of the cheaper, molded transparent varieties. Cast sheets are prepared by pouring the liquid resin monomer between glass plates and curing. A group of attractive patterned acrylic sheets are now available, with various surface details offering an interesting departure from a flat surface.

Styrene Resins

Styrene resins have become one of the most abundant, low cost thermoplastic materials. Copolymers of butadiene (75 per cent), and styrene (25 per cent) have fulfilled the great majority of synthetic rubber requirements, necessitating, during the war, an annual production of styrene alone close to 500,000,000 pounds. Aside from the rubber requirements, styrene possesses a number of characteristics which make it highly desirable as a plastic material.

Styrene

Raw Materials—Petroleum
Reagents—Ethylene gas, benzene
Products—Styrene monomer, polystyrene molding powder, sheets, rods, tubes, foils (extruded and cast)
Tradenames—"Lustron", "Styron", "Loalin"

Styrene, a colorless liquid boiling at 145 C (293 F), polymerizes to transparent substances, properties of which are dependent upon the conditions of polymerization. Ethylene, derived from cracked hydrocarbon gases, is passed through benzene in the presence of an aluminum chloride catalyst to yield ethylbenzene, which in turn is cracked at high temperatures to form styrene.

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + C_6H_6 \rightarrow \underset{\text{Ethylbenzene}}{C_6H_5 - CH_2 - CH_3}$$

$$C_6H_5 - CH_2 - CH_3 \xrightarrow{\text{Heat in iron tube}} C_6H_5 - CH = CH_2 + H_2$$

Ethylbenzene is pyrolyzed in some processes by mixing with superheated steam to yield styrene. Chlorinating the ethylbenzene and subsequent thermal decomposition in a nichrome tube will likewise yield HCl and styrene. Polymerization is accompanied by opening the double bonds in the reactive ethylene group to form a long chain macromolecule.

$$n(CH_2{=}CH{-}C_6H_5) \rightarrow \underset{\text{Polystyrene}}{-CH(C_6H_5)-CH_2-CH(C_6H_5)-CH_2-CH(C_6H_5)-CH_2-}$$

Clearer products are obtained in the absence of oxygen, particularly when the polymerization is conducted in mass by heating for several days at 125 C (257 F). A polymer with an average

molecular weight of about 125,000 appears to be the most generally useful material, though investigators such as Dr. Staudinger report molecular weights approaching 1,000,000 by slow, low-temperature polymerization. When it is desired to store styrene for long periods of time, polymerization inhibitors such as quinol are added.

Molding Compositions: Within the last few years the development and the application of polystyrene molding compounds have received much impetus from outside as well as within the plastics industry. These materials display excellent dielectric qualities, particularly at radio frequencies where other dielectric materials are unsatisfactory due to high dielectric loss factors. In consequence the radio industry has been one important outlet for these materials, which have helped to improve the high quality of the transmitting and receiving equipment. The negligible water absorption and resistance to acids should make the material ideal for equipments handling acids.

Molded as well as cast articles of polystyrene have a clear metallic ring when they are struck a sharp blow or dropped upon a hard surface. This distinguishes them from other thermoplastic materials. Cast polystyrene articles, while readily prepared by heating a large mass of material at 260-270 F for three to five days, are not as common as the molding compositions. Greater skill is required in machining or fabricating polystyrene than other thermoplastic materials.

Recent developments in styrene molding compositions have featured copolymers such as "Cerex" and "Plexene" which offer improved strength and temperature resistance. This is a noteworthy trend, because thermoplastic moldings have been excluded from many engineering applications due to their poor temperature resistance.

Sheets and Foils: Clear transparent sheets and foils are available in polystyrene. The sheets may be fabricated readily, like the acrylics, though they are much softer and are not as popular among fabricators of plastics. While the foils which were first developed had a notable drawback in extreme brittleness, recent developments in extruded foils, involving mechanical stretching after extruding, have done much to make a more mechanically acceptable product. The foils find their greatest utility as electrical insulation. Resistance to water vapor permeation, however,

is not as great in polystyrene foils as in other materials.

Polydichlorostyrene: Developed for better temperature resistance than polystyrene, polydichlorostyrene has lost none of the effectiveness of its predecessor as an insulating material, especially at high frequencies, where it maintains a constant power factor over a broad range. Its heat distortion temperature of 235 F is considerably above polystyrene's 170 F ("Styramic" HT). Higher injection-molding temperatures are necessary, though the product is quite stable. In applications to electronic equipments polydichlorostyrene has exhibited good form stability in its resistance to heat from tubes and transformers. The presence of chlorine renders the compounds resistant to burning and makes them self-extinguishing.

Styrene Copolymers: Aside from the all important butadiene copolymer, styrene is capable of copolymerizing with a vast number of other synthetic resin monomers. One of these, with divinyl benzene, has permitted raising the heat distortion temperature to around 250 F and still permitting conventional injection molding. Numerous crystal holders have been molded from these copolymers for application in high frequency work. These compounds closely resemble polystyrene. Plasticizers seldom are used with polystyrene, though it may be pointed out that chlorinated diphenyls are mechanically acceptable. Partially polymerized styrene is extensively employed as a toughening agent in polyester resins. A rubber-like copolymer is formed through reaction with butadiene ("Styralloy"). By increasing the ratio of styrene to butadiene, stiffer products are developed.

Styrenated Oils: Another development of particular note to coating manufacturers is the appearance of styrenated oils. By cooking styrene and methyl styrene with drying oils some very useful constituents for coatings have been obtained.

Polyamides

The polyamides represent a family of synthetic resins possessing widely different physical and chemical properties. They have become well known in the form of fine and coarse filaments ("Nylon"), for use in stockings, tooth brushes, parachutes, filters, and paint brushes. More recently they have found important uses as molding compounds.

Polyamides

Raw Materials—Coal tar, air and water
Reagents—Diamines (hexamethylenediamine), and dicarboxylic acid (adipic acid)
Products—Molding compounds, extruded monofilaments, textile products

In his development work on the polyamides, Carothers produced many types of synthetic resins, as there are many diamines and dicarboxylic acids capable of reaction to form the polymers. In the beginning, interest centered on the fiber-forming polyamides of high melting point. Polyamides are formed from the interaction of diamines upon dicarboxylic acids. Representing a diamine by the following formula: $H_2N—G—NH_2$ and a dicarboxylic acid by the formula: COOH-G′-HOOC, where G and G′ are hydrocarbon radicals, a long-chain polymer is formed of the following structure.

$$—NH—G—NH—CO—G'—CO—NH—G—NH—CO—$$

Adipic acid and a diamine, for example, are reacted in a stainless steel kettle to form a nylon salt. These solutions then are concentrated and polymerized in an autoclave and, at the proper point, the autoclave is opened and the material flowed onto a revolving wheel to harden in a shower of water. These are chipped into flakes which are blended together and purged of oxygen. After remelting down and filtering, the compound, which has a rather sharp melting point above 500 F, is forced through a spinneret. By traveling through rolls of different speeds, the filaments are cold-stretched and twist-set in a steam oven. Tensile strengths above 50,000 psi are obtained. These filaments have a decided resiliency which is imparted to tow ropes and parachute lines prepared from these compounds.

Molding Compositions: While polyamides are capable of operation up to temperatures of 400 F, their ASTM heat-distortion point is low (about 150 F.) Physical properties are closely dependent upon moisture content and the prevailing temperature. When molded parts require considerable toughness, high softening temperature and the ability to be safely injected in thin sections, the nylon molding compounds have proved feasible. Special designs are required in the nozzle and plasticizing chamber of the

injection molding machine to accommodate the material. Compared to the better known cellulose plastic injection-molded thermoplastics, the nylon molding compounds are tougher and more dependable over a much broader ranger of temperatures. A non-rigid grade of polyamide developed abroad, found employment in various machines. This material was caprolactam, prepared from cyclohexanone.

The polyamides are inherently resistant to most organic solvents and plasticizers, though they may be dissolved by molten phenol, resorcinol, or formic acid. More chemically compatible polyamides have been prepared from ethylene diamines and from soya-bean-oil fatty acids ("Norelac"). These have been developed for coatings and adhesives.

Newly Developed Synthetic Resins

Silicones: Among the plastics developed to date having highest temperature resistance, silicone resins have opened a new field of plastics in chemistry. These plastics have many new and unusual characteristics which are of basic interest in the design of various machines. These organo-silicon oxide polymers now are available in several physical forms including fluids which have little change in viscosity over wide temperatures, greases, insulating resins, rubber-like varieties, and thermosetting materials. Their heat stability, inertness, and electrical properties are, in large part, due to the silicon-oxygen-silicon-structure.

Silicone resins are prepared from silicon tetrachloride, magnesium metal, and organic chlorides, following the Grignard reaction, which is somewhat difficult to carry out on a commercial scale. Methyl-magnesium-bromide is reacted with silicon tetrachloride to produce, for example, mono and di-methyl silicon chlorides. These are hydrolyzed in turn to form silanols, which are capable of condensing within themselves to form resinous derivatives. Another method for preparing the alkyl-silicon chlorides is to pass an alkyl halide over powdered silicon-powdered copper at a high temperature. Methyl silicones are obtained in this manner.

$$CH_3 . Mg . Br + SiCl_4 \rightarrow CH_3 . SiCl_3 \text{ or } (CH_3)_2 SiCl_2$$

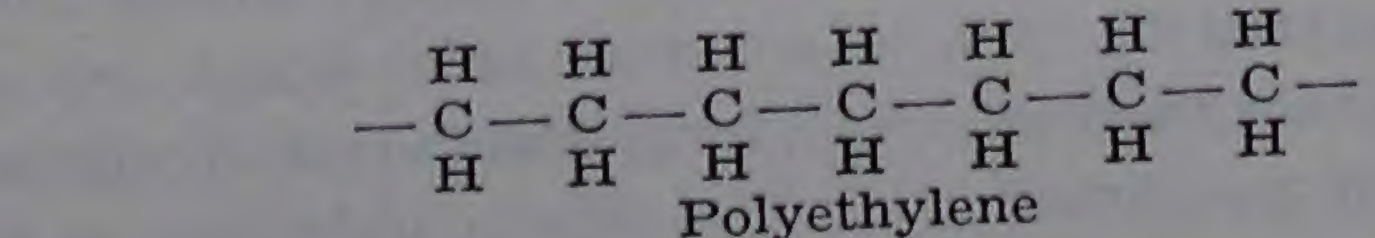
$$CH_3 SiCl_3 + 3H_2O \rightarrow CH_3 . Si . (OH)_3$$

$$CH_3 \underset{OH}{Si} OH + HO \underset{OH}{Si} CH_3 \rightarrow CH_3 \underset{OH}{\overset{OH}{Si}} — O — \underset{OH}{\overset{OH}{Si}} CH_3$$

Numerous side reactions ensue in the formation of the silicone resins, and considerable skill is required to direct the reaction toward the correct degree of cross-linkage. Many of the silicone resins appear as oils possessing a high degree of viscosity stability with temperature. Characteristics are dependent upon the nature of the substituent introduced in the Grignard reagent and the molar proportions of ingredients. Aryl silicones are softer than the alkyl silicones, and various combinations may be effected through reactions of organo silicon chlorides with other Grignard reagents. Suffice it to point out, however, that a new horizon looms in the field of silicone resins which possess high temperature stability and the ability to operate at temperatures in excess of 400 F. In *Fig.* 9 are shown two motors of the same horsepower rating. The smaller motor has been insulated with high-temperature-resistant silicone resin and fiberglas, and is capable of operating at a much higher temperature, hence its greater horsepower/weight ratio.

Liquid silicone resins readily wet clean, dry surfaces of glass, ceramics, and metals, making them water repellent to a marked degree. This may be accomplished also by exposing the surface to the vapor of methyl chlorosilane which may be reacted with water vapor to form a silicone. These resins have also shown promise as a high-temperature lubricant for machine bearings.

Polyethylene: A tough, flexible polymer has been prepared direct from ethylene gas through a high-temperature, high-pressure polymerization process in the presence of a trace of oxygen. This material possesses outstanding electrical properties and unusual resistance to water and water vapor permeation. The chemical structure of polyethylene is relatively simple, and the polymer substantially unsaturated:



Polyethylene

The high-molecular-weight polymer melts rather sharply above 100 C, permitting flame spraying and the development of tough, chemically resistant coatings. The material is soluble in boiling xylene, though at room temperature it is resistant to most chemicals. In commercial forms, various sheets, molding materials,

and extruded shapes have been produced. The specific gravity of the material is quite low, averaging about 0.92 at 20 C. During extrusion, the material may be cold stretched to materially increase its tensile strength. Polyethylene may be compounded with

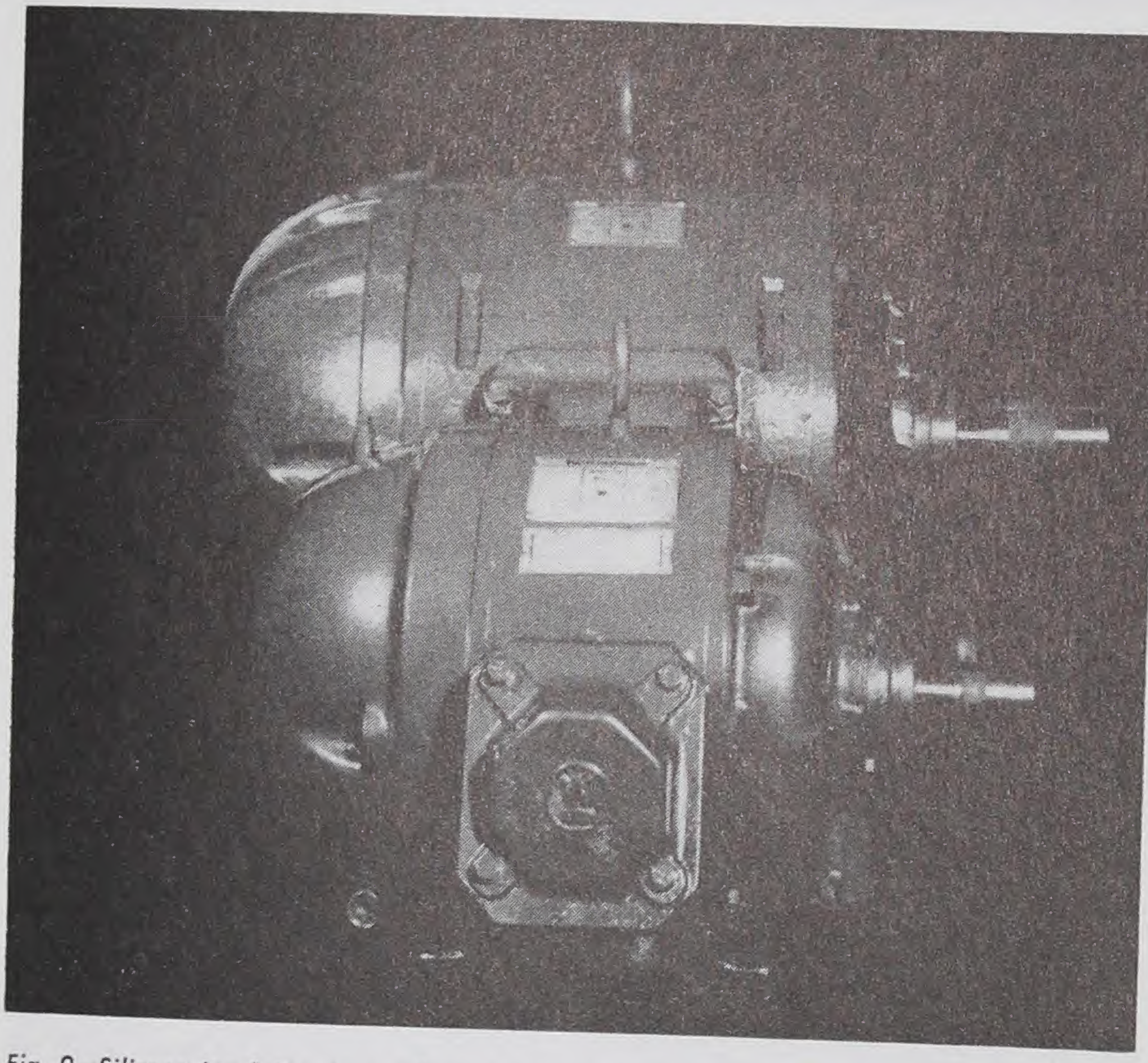


Fig. 9—Silicone insulation in small motor permits it to operate at increased temperatures. Result—without increased operating speed, it develops same power as larger motor

polyisobutylene to increase its elongation. Polyethylene will undoubtedly be best known for its chemical inertness, and its splendid properties as a dielectric at high frequencies. It lends itself to the design of food processing machines and equipment, as well as radar and electronic apparatus.

Polyisobutylene: A major constituent in one of the more important synthetic rubbers, ("Butyl" rubber), isobutylene has shown considerable promise as a flexible, rubber-like elastomer. Available in forms ranging from viscous fluids of relatively low molecular weight to tough, elastic solids of high molecular weight,

isobutylene has found increasing utilization as an important plastic in the field of coatings and adhesives. Manufacture of the material from various mixtures of butenes takes place at low temperatures in the presence of boron tri-fluoride as a catalyst.

Furfural and Furfuryl Alcohol Resins: Furfural, obtained as a by-product in steam distillation of acidulated corn cobs or oat hulls, has long been recognized as a useful organic solvent. This aldehyde, as well as its hydrogenated derivative, furfuryl alcohol, recently has been made commercially available in the form of liquid resins useful as adhesives and impregnating compounds. The resins are dark in color and show unusual penetrating and wetting properties. They show considerable promise as impregnants for plaster of paris, toughening up patterns and tools to hard, durable materials. Cold-setting adhesives prepared from these resins are among the strongest ever developed, and well suited to the bonding of various plastics and rubbers.

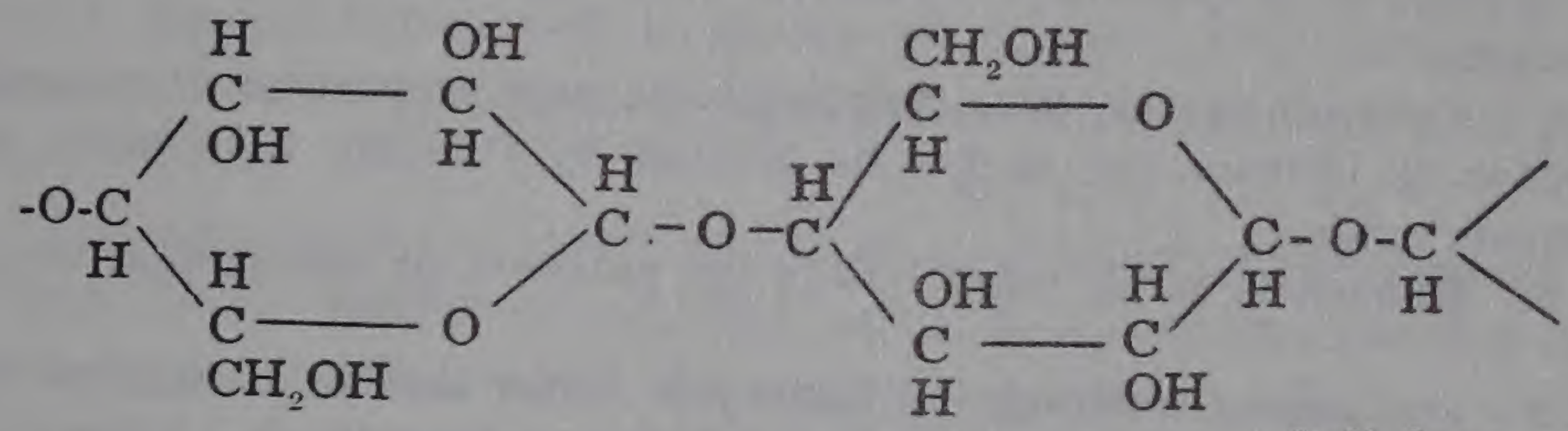
Polytetrafluoroethylene: Another important high-temperature-resistant material which appeared during 1946, is polytetrafluoroethylene ("Teflon"). This resin has shown remarkable chemical resistance, being resistant to all concentrations of commercial acids, including boiling aqua regia. Material of this nature will influence the design of chemical processing equipment and high-temperature mechanical rubber goods. Specific gravity of 2.1 to 2.2, high elongation, low-temperature flexibility, and good flame resistance feature this material.

Olefin-Sulfur Dioxide Resins: A potentially important new group of low-cost thermoplastic synthetic resins has been developed by the reaction of sulfur dioxide with various olefins such as propylene, n-butenes, and l-decene. Hard moldable varieties to rubber-like compounds have been produced. These materials are being developed by the Phillips Petroleum Co. Good chemical resistance is claimed for the polymers.

Plastics from Cellulose Derivatives

Resins discussed in the preceding paragraphs may be truly described as synthetic resins, inasmuch as they have been synthesized from raw materials which themselves are not resinous. Plastics from cellulose derivatives on the other hand are derivable from cellulose, which is a natural occurring polymer of high-mole-

cular weight. Cellulose, prepared from wood and cotton, is esterified or etherified to convert the material to heat fusible or soluble forms useful for preparation of artificial fibers, thin flexible films molding compositions, etc. Cellulose plays an important part in the constitution of the fibrous structure of the vegetable kingdom. The structure that has been assumed for the cellulose molecule $(C_6H_{10}O_5)_n$ is of a chain-like form, built up of betaglucose units. Chemical investigations, confirmed by X-ray analysis, show the following structure:



Cellulose

The cellulose chains are assumed to be arranged in the form of crystalline submicroscopic micelles in which intermolecular linkages are established between adjacent chains through secondary forces, whereas the strong primary bonds prevail between glucose units of the macromolecules. It is reported that the dimensions of natural cellulose micelles are roughly estimated by X-ray data at 50 × 50 × 500 angstroms. The miscelles thus are revealed to be about ten times as long as they are wide, lending themselves to orienting influences parallel to the axis of the chain. While the chain lengths vary considerably natural cellulose is attributed with 100 to 200 glucose units, with molecular weight averaging about 30,000 to 40,000, though reported as high as 120,000. The cross section of a fibril will contain many thousands of micelles, each consisting of many chain lengths. The micelle structure is useful in interpreting the swelling action of certain liquids on the cellulose, though the cellulose derivative may be insoluble.

Cellulose Nitrate: The cellulose nitrate plastics date their origin and introduction to commerce as early as 1869. In one of their earliest forms they were called celluloid, though many trade-names are now in existence for these materials. The materials have found extensive application in solid form and as lacquer surface coatings. Conversion of the cellulose into cellulose nitrate (nitrated cotton) is a highly specialized process and materials

manufacturers may find it cheaper to purchase cellulose nitrate in the preparation of various compositions. A typical procedure for preparing cellulose nitrate follows:

1. Selecting cotton linters which are the short fibers attached to seed after long ones are removed for cloth.
2. Purifying by treatment with sodium hydroxide solution and chlorine to remove certain impurities and natural oil content of fibers.
3. Washing thoroughly in acid water to remove traces of alkali.
4. Bleaching linters with chloride of lime and washing. Shredding and drying to a moisture content of 0.5 per cent. (Now ready for nitration.)
5. Controlling the time, temperature, and proportion of reagents, nitration is carried out as far as desired by treating with nitric and sulphuric acids.
6. Removing acids from linters by pressure or centrifugal wringers.
7. Successive washings by boiling in water and acid solutions will remove impurities from the nitrated cotton. Bleaching, washing, removing chlorine, washing, beating in pulp machines, washing, and blending batches for uniformity.
8. Dehydrating with alcohol.

One of the most important steps in the manufacture of cellulose nitrate is the nitration process. In this reaction the hydroxyl groups of the cellulose molecule are reacted upon and replaced by nitrate groups from the nitric acid. The presence of sulphuric acid will catalyze the reaction. The nature of the final product is dependent upon the degree of nitration for, with more advanced nitration, explosive materials are obtained. With 2.0 to 2.4 hydroxyl groups substituted, materials useful for engineering purposes are prepared. The reaction ensues in the following manner (it is assumed that full nitration occurs):

$$(C_6H_7O_2(OH)_3)_x + 3 \times HONO_2 \rightleftarrows \times (C_6H_7O_2(ONO_2)_3) + 3 \times H_2O$$

TABLE VI

Characteristics of Cellulose Nitrate

(As dependent on degree of substitution)

Product	Nitrogen content (per cent)	Typical length of macromolecule No. glucose units
Explosives	12.1 to 13.8	3000 to 3500
Lacquers	11.5 to 12.1	175
Plastics	10.5 to 11.5	500 to 600

Equilibrium is dependent upon the composition of the acid mixture, and adjustments in the nitrating conditions will give a wide range of substitution up to three nitrate groups. Properties depend upon the degree and uniformity of the substitution, and relative purity of the acid mixtures. Characteristics of typical cellulose nitrate products, including nitrogen content and macromolecule length are presented in TABLE VI.

The commercial cellulose nitrates are made available in a wide choice of viscosities (degrees of polymerization) for lacquers and films. In general, low-viscosity nitrocellulose is preferred for lacquer formulations, and a choice of degree of nitration is required to realize maximum compatibility with solvents and plasticizers.

The attainment of good physical properties which are so important to the utility of cellulose nitrate as an engineering material, is not realized until the material has been blended with a plasticizer. Camphor is employed as a plasticizer for cellulose nitrate because of its high solvent power for this material and because it renders the material mechanically acceptable. Other cellulose esters have supplanted cellulose nitrate in many engineering applications in recent years, inasmuch as they lack the inflammability of these materials and exhibit greater permanency of physical properties.

Cellulose Acetate: The cellulose ester of greatest industrial importance as a plastic material is cellulose acetate. As in the case of cellulose nitrate, pure cotton linters are employed as a source of cellulose. The fibers first are pretreated and activated by the presence of glacial acetic acid and catalyst. Following this step the actual acetylation takes place on the addition of acetic anhydride with gradual solution, more acetic acid, perhaps a solvent such as methylene chloride, and a catalyst such as sulphuric acid. The temperature of the reaction is maintained at a relatively low limit, and after several hours the cellulose is transformed into a thick syrup. The reaction product then is fed to a hydrolyzer where the addition of a certain amount of water at the right temperature will precipitate the ester. The cellulose derivative is filtered and then allowed to season for a period of time. After drying to the right moisture content, a white floccular substance, insoluble now in acetone, and suitable for incorporation in plastics, safety film, and lacquers is obtained. Cellulose acetate

(acetylated cotton) is available for inclusion in thermoplastic compositions.

The chemical reaction involved in the preparation of cellulose acetate follows.

$$(C_6H_7O_2(OH)_3)_x + 3X\,(CH_3CO)_2O \rightleftarrows X\,C_6H_7O_2(OCOCH_3)_3) + (3X\,CH_3COOH)$$

Cellulose — Acetic Anhydride

Degree of acetylation is important in determining the characteristics of the final product. The theoretical triacetate is not as important commercially as products with a lower acetyl content which have greater solubility and are more suitable in plastic compositions. Higher acetyl substitutions are soluble in chloroform mixtures, while lower-degree acetylation substitutes are dissolved more readily by acetone mixtures. The selection of solvents for these materials, however, should be conducted on the basis of both the cellulose derivative and the plasticizer which are employed, because it is necessary that the solvent be effective on both.

The reaction products as a function of the degree of acetylation are presented in TABLE VII.

TABLE VII

Characteristics of Cellulose Acetate

(As dependent on degree of substitution)

Product	Acetyl groups as % of molecular weight
Cellulose triacetate	44.8
Cellulose diacetate	35.0
Plastics	36.5 to 38.5
Textile grades	38.0 to 39.4
Lacquers	37.5 to 39.5

Cellulose acetate is combined with plasticizers in the presence of solvents to attain the qualities so important to molding, and a toughness it otherwise would not possess. Well-known plastic materials such as "Tenite I," "Plastacele," "Lumarith," etc., are prepared from cellulose acetate. These materials are thermoplastic in nature and are suited for injection molding. Cellulose nitrate plastics, unstable in the presence of heat, are not suited for injection molding.

The water resistance of cellulose acetate is not as good as that of cellulose nitrate, and to improve this quality, a water-resisting higher acetyl-content (40.1-41.6%) acetate has been de-

veloped. Among the plasticizers most commonly used with cellulose acetate are methyl and ethyl phthalates, methyl phthalyl ethyl glycollate ("Santicizer M-17"), and triacetin.

Mixed Cellulose Esters: Mixed cellulose esters, prepared by reactions similar to those previously described, are used extensively as molding compounds and in the formulation of hot-melt stripping compounds. The mixed cellulose esters are prepared by activating the cellulose fibers in glacial acetic acid, followed by acid mixtures of higher aliphatic acids and acetic acid. As for the other cellulose esters, properties are dependent upon the degree of substitution, as well as the average degree of polymerization. The cellulose acetate-butyrate most generally used is a material of about 14 per cent acetyl content and 36 per cent butyrl content, or, in terms of substitution, 1.1 acetyl, 1.6 butyl, and 0.3 hydroxyl units per C_6 unit. In general, the chain length of these esters varies between 250-350 degree of polymerization.

Cellulose acetate-butyrate ("Tenite II") possesses good injection molding properties, requiring a lesser degree of plasticization than cellulose acetate to attain the same degree of flow. It is also extensively employed as extruded strips and tubes for numerous purposes. Better dimensional stability is exhibited by this mixed cellulose ester and high acetyl-content cellulose acetate under changing humidities. In recognition of the growing interest in cloth-reinforced laminates and the possibilities of deep drawing them into tough laminated structures, cellulose acetate and acetate-butyrate have been friction-calendered on cloth bases and welded together into a composite structure under heat and pressure.

Cellulose Propionate: The latest addition to the family of cellulose derivatives is cellulose propionate ("Forticel"), prepared by the action of propionic anhydride upon cellulose. In physical properties, this plastic resembles cellulose acetate-butyrate more than cellulose acetate, requiring less plasticizer to achieve the same degree of flexural rigidity. High impact strength and low water absorption characterize the molded products. Also good molding and welding properties have been displayed in the field. Whereas it can be successfully mixed in all proportions with cellulose acetate-butyrate, it will not mix satisfactorily with the acetate by itself.

Competitive to cellulose propionate is the mixed ester cellulose

acetate-propionate ("Tenite III"), also developed for tough, dimensionally stable molded parts. Properties and applications are similar to the other cellulose esters.

Sheet, Rod and Tube Stock of Cellulose Plastics

An important branch of the cellulose plastics industry is the manufacture of sheets, rods and tubes. Cellulose acetate and cellulose nitrate constitute the major proportion of this business. Starting with nitrated or acetylated cotton (prepared by methods described in the preceding pages), plasticizers, solvents, and sometimes dyes, are blended together in a large kneading or dough mixing machine until a homogeneous blend of ingredients is obtained. Enough solvent and plasticizer must be present to allow the material to be readily workable and easily mixed.

After mixing, the dough-like mass is filtered under the action of a heavy hydraulic press which forces the material through fine-mesh screens supporting cloths, through a die plate with fine openings. The amount of solvent present may be reduced by working the mass in a vacuum mixer. Otherwise, solvent is removed by working on hot mixing rolls where dyes may be added if desired. The material is cross-cut by the operator and folded back to insure uniform distribution and blending. After this operation, slabs are removed from the mixing rolls and stacked in presses. Under heat and pressure, large blocks several inches thick are formed (see Flow Sheet, *Fig.* 10).

There is still sufficient residual solvent to permit further operations. The large blocks are removed to slicing machines where molding blanks or sheets may be sliced to size. The sliced sheets are placed in seasoning rooms for a length of time which may be several weeks, depending upon their thickness. Upon removal from the seasoning room they are wiped off and press-polished between highly polished sheets under heat. This straightens the sheets and gives them their smooth glossy finish.

Some of the thin sheet stocks (0.020-inch and thinner) are prepared by extruding continuously from fine orifices, festooning the sheet within a seasoning chamber. They usually are transparent and are employed for packaging and for electrical insulation. When formed, as in the manufacture of transparent containers, the slicing marks, which may appear on sheets cut

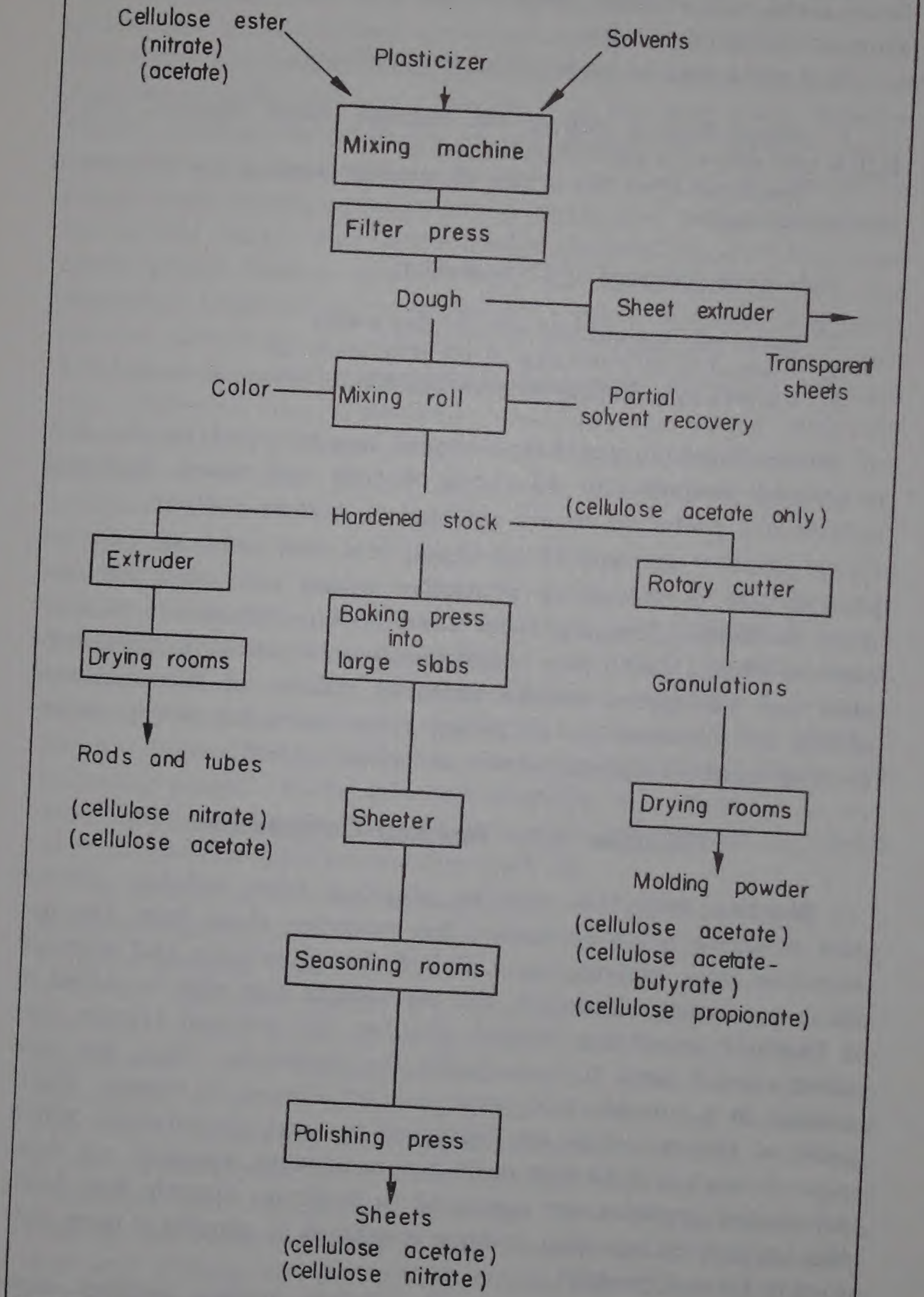


Fig. 10—Flow sheet for manufacture of cellulose ester plastics

from slabs, are entirely absent. Extremely thin films are cast from solutions of plastics.

Rod stock may be prepared by two methods:

1. Sliced from a slab of the cellulose plastic material with a hollow tool shaped to the size of the rod, or
2. Extruded from the orifice of a screw stuffing machine into a continuous length.

Tubes are prepared by three methods:

1. Extruded continuously without any seams
2. Formed by butt-welding of flat strip stock, or
3. Formed by wrapping strip stock helically around a mandrel.

Many fountain pen barrel stocks are prepared by the last-mentioned method. In all cases of rods and tubes, seasoning periods are preferred to aid removal of solvent content.

Color: Sales appeal of sheet, rod and tube of cellulose plastics lies in the many attractive colors and color combinations available. Ranging from clear, transparent sheets to pearl essence effects, there is a kaleidoscopic selection of mottled, striated and variegated colored patterns. Many of these unusual effects are obtained by preparing large slabs for slicing or extruding, in which different strips are spaced at will.

Cellulose Ester Molding Compositions

Molding materials may be prepared from cellulose acetate and cellulose acetate-butyrate by removing them from the hot blending rolls, grinding in a Ball & Jewell grinder and allowing them to season. However, the ingredients may also be mixed in a Banbury mixer for several minutes, the internal friction creating enough heat to homogenize the materials. They are then ground in a suitable mill, screened and allowed to season. While most of the materials are furnished in large granulations which pass through a 3/16-inch-mesh screen opening, specially cut cubical-shaped granules are employed to facilitate granule flow down the hoppers of injection molding machines to provide a more uniformly formed product.

While cellulose nitrate and cellulose acetate molding compositions have been adaptable to compression molding operations,

only the latter has been suited to injection molding. The requirements upon molding compositions for thermoplastic materials differ appreciably from those for thermosetting compositions such as phenolic and urea plastics. In the first place, thermoplastic molding compositions do not undergo a "curing" period during molding analogous to those experienced by thermosetting resins when physical properties are developed during polymerization of the resin. The thermoplastic composition, however, must attain proper flowing qualities upon the application of heat and pressure. Contributing in a large measure to these properties are the plasticizers in cellulose ester compositions. The plastic flow requirements are particularly important in injection molding. However, the plasticizers commonly associated with cellulose nitrate are unstable due to the high temperatures. In fact molding of cellulose nitrate is limited, though hot swaging operations are in more common use.

Physical properties developed by cellulose ester molded pieces depend to a large measure upon the proportion of plasticizer to cellulose derivative. Unlike thermosetting compositions, it is not necessary to add fibrous fillers for mechanical reinforcement. Through the use of the proper plasticizers, cellulose derivatives inherently possess adequate resistance to shock. Being thermoplastic, however, the cellulose derivatives have relatively low softening points. While this characteristic is a drawback in certain engineering applications, the materials have opened new fields of application by injection molding methods.

A number of molding compositions have been developed with different degrees of flow to make possible the injection molding of parts ranging from buttons to antenna post housings. Generally the consumer desires a product with as high a shear, tensile, and flexural strength as possible; these properties are improved with harder degrees of flow. On the other hand, the custom molder prefers a softer composition which may be handled with less difficulty by the injection molding machine. A compromise generally is effected between the requirements of good production and engineering. For the more important thermoplastics, the various degrees of flow recently have been standardized and defined by the ASTM standards. These grades are achieved through the compounding of different proportions and types of plasticizer with the cellulose acetate or acetate-butyrate

and cellulose propionate, and range from hard types (Grade H) to soft types (Grade S). Various grades and typical end uses are cited below.

1. Grade *VH*—very hard—adapted to special mottled compositions
2. Grade *H*—hard—for slabs and special uses
3. Grade *MH*—medium hard—high heat distortion point, for novelties.
4. Grade *M*—medium—for novelties, general optical
5. Grade *MS*—medium soft—excellent impact resistance, for general applications
6. Grade *S*—soft—thin objects, good welding, for boxes, etc.,
7. Grade *VS*—very soft—good welding, high gloss, for very thin-wall moldings requiring a long flow.

ASTM Specifications have been prepared for cellulose acetate molding compositions (D-706) and cellulose acetate-butyrate compositions (D-707). The types and flow designations (obtained from ASTM Specification D-569) are shown in TABLE VIII.

TABLE VIII

Cellulose Acetate			Cellulose Acetate-Butyrate		
Type	Grade	Flow Temperature	Type	Description	Flow Temperature
I General-purpose	MH	300-315 F	I	Good dimensional stability	325-339 F
	M	290-300			
	MS	280-290	II	Good dim. stab. and fair impact qualities	307-321
	S	260-280			
II Heat-resistant	VH	330-345	III	Moderate dimen. stability, mod. impact and toughness	293-307
	H	315-330			
III Impact-resistant	MS	280-300	IV	Good impact and toughness	279-293
	S	270-280			
	VS	260-270	V	High impact and toughness at 32 F	265-279
	SS	250-260			
IV Moisture-resistant	VH	330-345	VI	Good impact at low tem.	253-267
	H	315-330			
	MH	300-315			
	M	280-300			

In the specifications of TABLE VIII the flow temperatures are primarily for the information of the molders, rather than an aid to engineering design. However, they do indicate the interrelationship between the molding qualities and the intended applications. Lower flow temperatures are obtained in general by a higher proportion of plasticizer, resulting in lower tensile strength and increased elongation and creep at room temperatures.

Cellulose Ether Compositions

Ethyl Cellulose: Useful plastic materials are prepared by the etherification of cellulose. The best known are ethyl cellulose and benzyl cellulose. The ethyl (C_2H_5) radical or benzyl (C_6H_5) radical are linked to the cellulose molecule through oxygen to form what is known as an ether. In the preparation of cellulose ethers, the cellulose is allowed to swell in an 18 to 20 per cent sodium hydroxide solution to form sodium cellulose. The alkali is removed later, by pressing.

$$(C_6H_9O_4OH)_x + X\,NaOH \rightarrow \times\,(C_6H_9O_4 - ONa) + XH_2O$$
Sodium Cellulose

Sodium cellulose is treated further with alkylating agents such as alkyl halides and sulfates. Ethyl chloride, prepared from pure ethylene and hydrochloric acid in the presence of an iron oxide catalyst, will convert sodium cellulose to ethyl cellulose. Methyl cellulose and benzyl cellulose are prepared in like manner with methyl chloride and benzyl chloride used respectively. A close control of time, temperature, pressure, and reagents is maintained as products vary in accordance with the degree of substitution for sodium, which may be linked at more than one hydroxyl group in the glucose unit. A typical reaction of ethyl chloride upon sodium cellulose is:

TABLE IX

Characteristics of Ethyl Cellulose

(As dependent on degree of substitution)

Qualities	Ethoxy groups % of molecular weight
Wide solubility and compatibility	48.0 to 49.5
Suited for plastics	45.0 to 48.0
Least soluble, highest softening point	43.5 to 45.0

$$(C_6H_9O_4ONa)_x + C_2H_5Cl \rightarrow \times\,C_6H_9O_4OC_2H_5 + Na\,Cl$$

Then the product is dissolved in a solvent and precipitated by water. Benzyl chloride may be substituted for ethyl chloride in the preceding reaction. The effects of the degree of substitution are outlined in TABLE IX.

In addition, a softening point for the least soluble grade of

ethyl-cellulose is reported between 160 to 180 C (320 to 356 F). In the attainment of desirable physical properties, as with other cellulose derivatives, plasticizers are added. Solvents are not always necessary in blending the ethyl-cellulose, heat and mechanical working being sufficient.

Among the plasticizers employed in ethyl cellulose compositions are dibutyl phthalates, diethyl phthalate, tricresyl phosphate, castor oil, monophenyl phosphate, chlorinated diphenyl, etc. The proportions of plasticizers required for various compositions are as follows:

	Per cent
Compression Molding	10 to 20
Injection Molding	15 to 30
Extrusion	25 to 50

Compounding of ethyl cellulose materials is readily accomplished because of the excellent compatibility of these materials with plasticizers and solvents, and some manufacturers have been able to produce hot blends with a minimum amount of solvents. When solvents are required, however, as in the preparation of lacquers and adhesives, mixtures of aromatics such as benzene (80%) and alcohols (20%) are recommended.

One of the most interesting features of ethyl cellulose is its compatibility with a wide variety of natural and synthetic resins, and waxes. Various hot-melt combinations have been prepared from ethylcellulose-plasticizer-wax combinations. These castable hot-melts have given outstanding service in the manufacture of semirigid dies for forming metals, outlasting their lead or zinc alloy predecessors, particularly in drop-hammer work.

Ethyl cellulose does not embrittle as rapidly as the cellulose esters as temperatures are lowered, and its low-temperature flexibility has made it a useful material for nonstructural components in aircraft. The good adhesive properties of the material are apparent in its self-sealing properties and its application to low-pressure cloth laminates, and the development of contoured surfaces as on small boats. The material has also enjoyed good use as an extrusion compound and as electrical insulation in thin foils. As a thin foil it is much more dimensionally stable and dielectrically acceptable than other thin foils of cellulose plastics.

Methyl Cellulose: Up to 6 or 7 per cent methyl cellulose may be dissolved in water to produce useful thickening agents or

dispersing agents. Sometimes they are blended with water miscible proteins or starches for adhesive purposes. Films deposited from methyl cellulose have also been used to coat paper and improve its gloss. As a thin film it is quite resistant to greases and oils.

Sodium Carboxymethyl Cellulose: Sodium carboxymethyl cellulose, prepared from reactions of chloroacetic acid and sodium hydroxide on cellulose, will dissolve in hot as well as cold water. It is commercially available in several viscosity types, ranging from 25 to 1500 centipoises for 1 and 2 per cent aqueous solutions. It has also served as additives to proteins and starches, and is used in creaming latex, ceramics, and various leather and paper finishes.

Hydroxyethylcellulose: Another water-soluble cellulose ether of note is hydroxyethylcellulose ("Cellosize"), which has seen service as a sizing agent. It is also being used to thicken aqueous emulsions of synthetic resins.

Regenerated Cellulose

Regenerated cellulose sheets (Cellophane) and woven goods (Rayon) are classified as organic plastics, because they undergo those chemical treatments so necessary to convert them to useful man-made materials. The chemical empirical formula for the final product is the same as for natural cellulose ($C_6H_{10}O_5$). As in the formation of ethyl cellulose, sodium cellulose is first prepared. After the sodium cellulose has aged, it is treated with carbon disulphide to form the following:

$$C_6H_9O_4.O\,Na + CS_2 \rightarrow C_6H_9O_4\,O\,CS\,SNa$$

Sodium Cellulose Xanthate.

Sodium cellulose xanthate is dissolved in sodium hydroxide, mixed and filtered, to yield a syrupy mass known as viscose. After a ripening period it is suitable for forming transparent films or viscose rayon. This is accomplished by forcing viscose through narrow slots or orifices into an acid-coagulating bath containing sulphuric acid and sodium sulphate. A desulphurizing and bleaching process may follow to leave an industrially useful material. Other types of artificial silk are prepared by cuprammonium, nitrocellulose and cellulose acetate processes.

Cellophane sheets generally are compounded with a small amount of glycerol to give them added flexibility. Special water-resisting grades of Cellophane also are available in which a thin coating of cellulose nitrate has been deposited on the outermost faces of the sheet. A new interesting product was developed at the start of the Second World War from regenerated cellulose. This was known as "Bubblfil" and consisted of an extruded rod with expanded bubbles approximately every ¼ inch. When assembled into a large bundle, a low-density, easily floatable mass was obtained.

Starch

Though not a cellulosic plastic, starch resembles cellulose because of the chemical identity of the molecular structure ($C_6H_{10}O_5$). It has enjoyed extensive adaptation as a paper sizing agent and as a low cost vegetable adhesive. High-strength adhesives formulated upon a maximum amount of unconverted starch have been successfully used in wood bonding. Recent efforts in developing starch esters, particularly the starch esters of amylose and not amylopectin, show possibilities in the field of plastics.

Lignin Plastics

In recent years, governmental agencies such as the Forest Products Laboratory have devoted much time to research on wood, cellulose, and lignin. Some of the investigations have led to the development of commercially useful materials. Lignin, present in wood to approximately 25 to 30 per cent, has been utilized in the preparation of molding and laminated compositions. Though the chemical constitution of lignin is still in question, recent X-ray studies of extremely pure lignin reveal a crystalline structure, a result contrary to conclusions pointing to lignin as an amorphous substance. Considerable differences are noticed in the lignin as obtained from various sources. When destructively distilled with alkali, hydroxyl groups are formed that are phenolic in nature. Treatment of cellulosic products, such as waste wood and sawdust in which the lignin content was increased, led to the development of a promising low-cost plastic material. Addition of plasticizers such as aniline lower the softening point of the lignin.

Molding compositions have been prepared which form hard, solid plastics under pressures of 3000 psi and at a temperature of 155 C (311 F). However, most lignin plastic molding compounds require some cooling before they may be safely ejected from the mold. They have not possessed the high quality of the present phenolic types, and generally the lignin plastics offered commercially have incorporated a small amount of phenolic constituents therein.

In the preparation of moldable lignin plastics, efforts have been directed toward the removal of hemicellulose by a digesting operation. Presence of hemicellulose increases water absorption and hinders the development of good flow properties during molding. While paper manufacturing is directed toward removal of much of the lignin through alkaline digestions, the manufacture of lignin plastics is conducted in an acid medium and the percentage of lignin enriched.

Maple sawdust is hydrolyzed under pressure in one well known process with three per cent sulphuric acid and the solid material freed from liquor and dried. To this is added 8 per cent furfural, 8 per cent aniline, and 2 per cent barium hydroxide in a wet mixing operation. A moldable composition with good physical properties is formed. Of course, the nature and quality of lignin depends a great deal upon the source of the cellulose. The fibrous mass is rich in lignin and cellulose, and hemicellulose is converted to a form in which it may be washed away.

At least one manufacturer has produced an important moldable plastic from bagasse ("Valite"), which has good molding qualities and low cost as its special merits. Another composition, "Lignolite", comprises a laminated structure of lignin enriched cellulose fibers. Good mechanical properties are possessed, though it is not recommended for use at high temperatures because of a tendency to blister. Hope is also entertained for a number of promising lignin esters in the plastics picture.

"Masonite" may be correctly described as a lignin plastic. In one process, chips from the Southern pine are loaded into an explosion chamber which is brought to a pressure as high as 1000 psi with superheated steam. After an interval of several seconds, the pressure is released suddenly and the chips exploded into a fibrous mass. After thorough wash, the pulp is formed into thick sheets in a continuous paper-forming machine. The

exploded chips contain a high percentage of lignin activated by the explosion process. The sheets are pressed and heat tempered into a wide variety of low-cost building materials extensively used in industry. One product, die stock, is obtained by pressing at a temperature of 165 C and a pressure of 2500 psi. Individual layers are bonded together with the aid of a phenolic film. The die stock competes favorably with laminated plastics in certain applications, where good mechanical strength and low cost prevail.

Plastics from Natural Resins

The numerous natural resins and their derivatives were tabulated earlier in this chapter. Rosin and its esters, bitumen, and shellac are most important in the plastics industry. While most natural resins are truly organic plastics in the sense that they may be molded to shape, they suffer in comparison with synthetic resins and cellulose derivatives as far as general usefulness is concerned. In the first place they are subject to variations, being natural in origin. Secondly, they are not of very high molecular weight, as evidenced by their sharp melting point and lack of toughness in a pure state. Natural resins are prepared as useful plastic materials by compounding them with the proper combinations of fillers and plasticizers, or they may be employed to augment some synthetic resin or cellulose derivative.

Rosin: Pure rosin (abietic acid) is best known to the surface coating industry, imparting oil solubility to certain thermosetting synthetic resins. The material is obtained by naphtha extraction of waste pine wood. It has long played a prominent role also as a sizing agent and adhesive component. Numerous esters prepared from rosin, hydrogenated rosin, or polymerized rosin ("Abalyn", "Hercolyn", "Staybelite", "Polypale" resin, etc.) are attracting much interest for their versatility and promise as liquid and semisolid plasticizers. Another natural resin, "Vinsol", described as the gasoline insoluble portion obtained from pine wood resin has an advantage in low cost (about 3 cents per pound) and usefulness as an extender for phenolic resins. Numerous laminated parts have been prepared with the aid of this resin. Another important use is in the manufacture of Portland cement, where the inclusion of a very small percentage of "Vinsol" has aided air entrapment during processing.

Shellac: Shellac is obtained from an insect secretion found in India. Chemically, it consists of hydroxy-carboxylic acids, partially combined with lactones or anhydrides. The presence of a small amount (5 per cent) of hard yellow wax, which assists flowing qualities, has been identified. Commercial shellac is separated into two fractions by ether extraction. The ether soluble fraction, being about 70 per cent, is pure lac resin.

When shellac is warmed, condensation reactions take place within the molecule with the evolution of water. The softening point of the material is raised until a difficult fusible state is obtained on repeated heating, establishing the basis for classifying the material as slowly thermosetting. Acids and nitrogen-containing compounds are regarded as accelerators for polymerization-condensation reactions, leading to hardening.

The widespread use of shellac as a surfacing agent, particularly on wood panels is well known. Employing inexpensive alcohol solvents, it is used extensively in varnishes, leaving hard, glossy surfaces, that will withstand much abuse. It is also resistant to tracking on insulators in the presence of power arcs. Carbonization of the surface will not readily take place, as with the phenolics in such electrical applications. Available in numerous low-cost molding compositions, it is applied to many articles. However, there are temperature restrictions, for the materials have relatively low softening points if not fully converted to a thermosetting material.

A wide variety of molding compositions has been prepared from the natural resin shellac. In fact, some of the first molding compositions ever to be made used a shellac binder. The largest consumption of shellac molded products is in the phonograph industry, with a production well in the millions. Laminated paper and mica insulating sheets with a shellac binder are employed in electric appliances. Shellac has good resistance to arcing, a factor in its favor in molded articles.

Large proportions of finely divided fillers are added to shellac molding compositions to lessen the cost of the molded article and maintain desirable mechanical qualities. Included as fillers are china clay, rock flour, slate flour, etc. For added shock resistance, a small amount of fibrous filler is also added. Copal, another natural resin, may be added to cheapen the shellac mixture. As with synthetic resins, the shellac molding compositions

may be prepared by the wet process in large mixtures or by a dry process on hot mixing rolls.

Bitumen: Bitumen is a term applied to certain naturally occurring complex, pyrogenous hydrocarbons insoluble in water but soluble in carbon disulphide and benzene. They are black in color and of varying hardness and volatility. Asphalt, a species of bitumen obtained from petroleum residues, has been employed in molding compositions. Closely associated are various fusible tars and pitches. In practical engineering use, bitumens are combined in various molding compositions and cold molded under high pressures, followed by baking operations. These compounds, using a bituminous substance of high-molecular weight, do not flow as readily as synthetic resins or cellulose derivatives, and must be fabricated with different techniques. Of theoretical interest is the influence of fillers on these compositions, as the tensile strength will increase up to a certain point on the addition of fillers. This is ascribed to the strength of adhesion between binder and filler, which is stronger than cohesion in the bitumen itself. In Chapter XIV bitumen base plastics are discussed at length.

Bitumen-base materials have in their favor low cost and availability. It is quite probable that rather than decline in use they will increase in use, particularly when modified with other materials which give them better temperature stability.

Protein Plastics

A few protein materials are useful in the preparation of plastics. Most important is casein, though soyabean protein and zein (corn protein) represent other potential sources. Formaldehyde is useful for converting the protein substances into relatively hard materials.

Casein: Though among the lesser known plastics encountered by engineers and machine designers, casein plastics have attained considerable prominence as a decorative material for miscellaneous and novelty articles. Casein, the chief nitrogeneous constituent of milk, is a phosphoprotein occurring as a calcium salt in combination with calcium phosphate. Commercially, casein is coagulated in milk to a jelly-like curd by rennin, an enzyne found in rennet (a by-product from the membrane of a calf stomach). Dilute mineral acids, such as hydrochloric and sulphuric

acid, or sour whey are sometimes employed in the coagulation of casein. The casein molecule possesses a complex structure, described by some as possessing a system of conjugated amino-acids (NH_2-R-COOH) where R represents the hydrocarbon portion of the molecule.

Various methods have been proposed and are employed in commercial production. Following precipitation, the casein is washed, filtered and pressed dry. At this stage it may be ground in the mill to proper granular size, and then thoroughly mixed with plasticizers and dyes in a dough machine. Further blending may be obtained by squirting the mass through small holes in die plates. In some processes a considerable quantity of paper pulp is added to promote mechanical strength. Casein is extruded into final form, and then undergoes a hardening process by immersion in formaldehyde. It has been suggested that hardening proceeds as a result of condensation of the aldehyde group with the amino groups, not dis-similar to that which ensues in the preparation of urea plastics. Casein is not available as a molding powder, and competes with other materials primarily on the basis of price. Buttons and buckles comprise the biggest uses for casein plastics. Button blanks after shaping, may be hardened by immersion in formaldehyde.

Casein adhesives have long been standard in the wood working field, improved water resistance being obtained through the addition of slaked lime in the formulation. These adhesives have become the subject of extensive experimentation and important end uses have developed. Extruded fibers of casein have appared in recent years in woven dress goods ("Aralac"), which have competed favorably with other synthetic fibers.

Soyabean Protein: The largest market for soyabean protein at present is in the production of adhesives for the plywood field. Outstanding contributions have been made in this field by plywood interests in the northwestern part of the United States. Aside from adhesives applications, soyabean proteins have found limited uses in this manufacture of molded plastics, generally as extenders for the phenolic resins. Formaldehyde hardened soyabean protein appears to possess certain advantages over soyabean protein as a filler.

Soyabean oils have been employed as drying oils in the formulation of baked varnishes. In addition, various fatty acids de-

rived from these oils are compounded with diamines to prepare synthetic resins. Considerable activity has occurred in the manufacture of soyabean protein fiber, which gives every indication of joining the casein fibers in the field of dress goods.

Zein: Zein, an alcohol soluble protein derived from corn, has been the subject of much investigation for its potential uses in the plastics field. Like other protein plastics, it depends upon water as a plasticizer to improve its flow, though smaller proportions are required than for soyabean protein and casein. While its use as a molding material was proposed as early as 1921 (U.S.P. 1,365,607), it has been applied most extensively as a coating material for wrapping papers, developing more water resistance than shellac.

Equipments for Preparing Molding Compositions

Equipments and machines employed in preparing molding compositions from synthetic resins and cellulose derivatives depend upon the nature of the materials to be blended, their susceptibility to heat-hardening, and physical and electrical properties desired in the final products. Dry and wet processes are currently employed in the mixing of the resins with fillers, lubricants, dyes, hardening agents, etc., though dry processes are most widely used. The "dry method" eliminates the necessity for solvents and the provisions for their recovery. Where it is necessary to preserve the length of long fibers for shock-resisting molding materials or where a large amount of liquid or low-melting-point plastic are to be blended into the composition, wet processes may prove more acceptable.

Ball and Pebble Mills: In a ball or pebble mill the correct amount of charge is mixed with a certain proportion of small balls, and the mill revolved at a fixed speed. The ball mill is unlined or has a metal liner and uses metal balls, whereas the pebble mill is lined with burrstone or porcelain and employs flint or porcelain balls. For grinding and mixing phenolics, burrstone lined pebble mills with flint pebbles are popular. There are also water-jacketed steel mills with porcelain balls (*Fig.* 11) for grinding urea as well as phenolic plastics. Because urea plastics are sensitive to heat, the water jacket helps to maintain a uniform, lower temperature by conducting away the heat generated by in-

ternal friction. Porcelain balls used for grinding one colored compound may not be used for another color, without a thorough washing and cleansing.

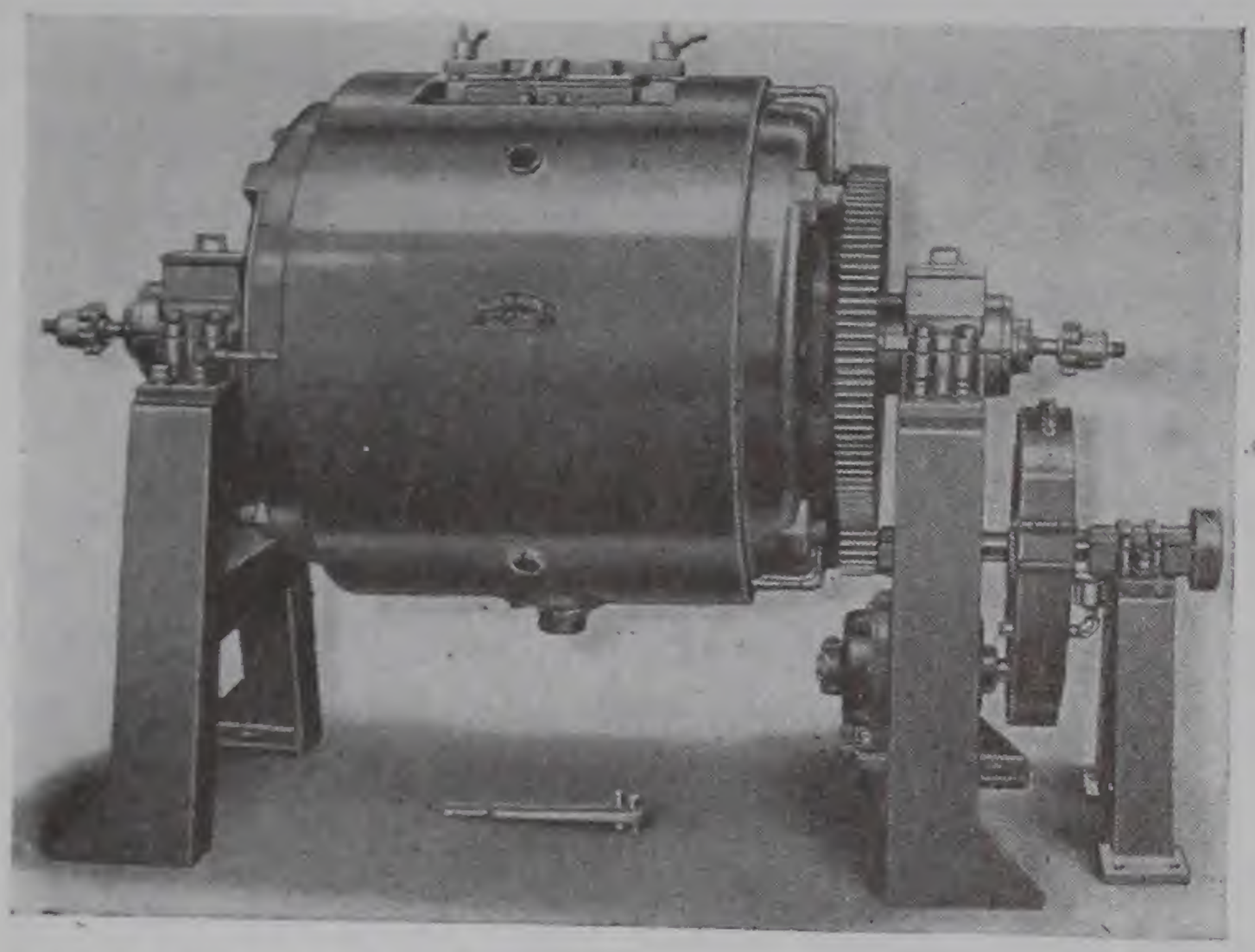


Fig. 11—Water-jacketed pebble mill for preventing excessive heat during grinding and mixing (P. Abbe Inc.)

For efficient grinding in the ball or pebble mill, the mill should be charged with 45 to 50 per cent of pebbles or balls, while the compound being ground should fill the voids between the balls and cover them to a slight extent. The mill is operated at a certain speed and for a definite time to obtain thorough dispersion. For example, broken-up stage A phenolic resin or urea formaldehyde condensation product from the drying oven are added to the rotating mill through a trap door and then the mill is allowed to rotate for a period of time. Lubricants, catalysts, fillers, dyes, etc., are introduced also and dry-blended with the resin which is gradually broken down to a fine powder. After a thorough mixing of all ingredients is obtained, samples are withdrawn from the mill, and the molding qualities are tested. If not up to standard, corrective measures are applied by adding further ingredients. Prolonged grinding will produce finer grades of molding composition. The charge then is screened and the light, fluffy molding powder stored in air-tight drums. If a more densified form of molding composition is desired, the molding powder must undergo a further operation on hot mixing rolls.

Hammer Mills: Hammer mills equipped with rotating hammers are widely used to grind the resin to a suitable degree of fineness, though not to the extent attained by the pebble mill. Often it is necessary to use a water jacket about the mill to avoid excessive temperature rise. Hammer mills have the rotating hammers mounted upon a vertical or horizontal shaft. The compositions are broken down to granular size by impact and may be permitted to fall to a bottom screened for the passage of particles smaller than the openings in the screen. Molding powders varying from 8 to 60 mesh generally are produced in mills, with a minimum of fines below 100 or 200 mesh.

Hot Mixing Rolls: Highly polished steel cylinders cored for the circulation of water or steam are revolved toward each other at slightly different speeds. They are designed so that the operator may adjust the horizontal gap between rolls to process the materials more satisfactorily in accordance with their bulk. Under the pressure and heat from the rolls the resins are melted and a hot blending action takes place in which there is a more intimate penetration of the resin into the remainder of the ingredients in the molding composition. This serves to densify the molding composition as well as produce a uniform blend. The revolving rolls also are equipped with heavy doctor blades which can be turned against the roll and cut or strip the mixture sticking to it, thus avoiding prolonged contact of some of the material closest to the hot rolls. The operators also may cross-cut the sheet of material with knives and fold it back into the mixture for more intimate blending.

Considerable care must be exercised in the hot blending of thermosetting compositions, as they have a tendency to "set up" and lose desirable molding qualities if subjected to excessively prolonged contact with the rolls. The time on the rolls varies, sometimes within the range of 5 to 15 minutes. Some phenolic resins will harden rapidly, and for them the mixing time should be as short as possible. Other soft resins, some of which cannot be processed satisfactorily in a grinding operation, can attain the entire blending on the mixing rolls. The resin, followed by lubricants, pigments, fillers, and then the hardening agents, are added until a uniform mixture is obtained. For reactive compositions, preliminary mixing as in a pebble mill will reduce the time required on the mixing rolls. The mixture when scraped off of the

mixing rolls may be passed immediately through blanketing rolls if molding sheets are desired. Otherwise, the cooled material is broken up into granular shape through an impact pulverizer or grinder.

Banbury Mixers: The masticator (Banbury) mixer has considerable application in the rubber and plastics industries, with high outputs and uniform results reported. They have been used in place of hot mixing rolls, and are cored and jacketed for the circulation of steam or hot oil. All working parts of the machine are fully enclosed and driven by a large motor. While previous mixing of the materials in a ball or pebble mill is not necessary when this machine is used, such preliminary operations may serve to reduce the time in the masticator mixer. As with hot mixing rolls, care must be exercised to avoid polymerizing the thermosetting resins to a too-advanced stage, otherwise the batch will be spoiled. For this reason thermosetting compositions are cooled as rapidly as possible upon ejection from the mixer.

There are two rotors, each of which has a tip or blade over which the stock must pass as the rotors revolve. The walls of the mixing chamber are concentric with the rotor, so that the bank of stock is acted upon by a tapered-wedge action due to the shape of the revolving blade. By forcing the material through narrow clearances to the wall, severe masticating action ensues. In addition a pressure ram applies positive pressure on the material fed through the hopper, forcing the charge into the kneading operation. This process has been applied to numerous synthetic resins and cellulose derivatives (see U.S.P. 2,056,793-4,5,6,7, to DuPont Inc., Oct. 6, 1936). It has been reported that mastication under positive pressure may be effected without the addition of volatile solvents, though it may require a longer period of time. A typical Banbury mixer is shown in *Fig.* 12. The chief benefits lie in high outputs within short periods of time.

Dough Mixing Machine: Always a difficult mixing problem is the blending of thick, dough-like plastic masses of material, such as may be necessary for cellulose derivative compositions. Thermoplastic material, softened by the addition of a suitable solvent, is blended with its plasticizers in a machine of this description. A stretching, folding, and kneading action takes place because of the limited flow of the ingredients of the composition.

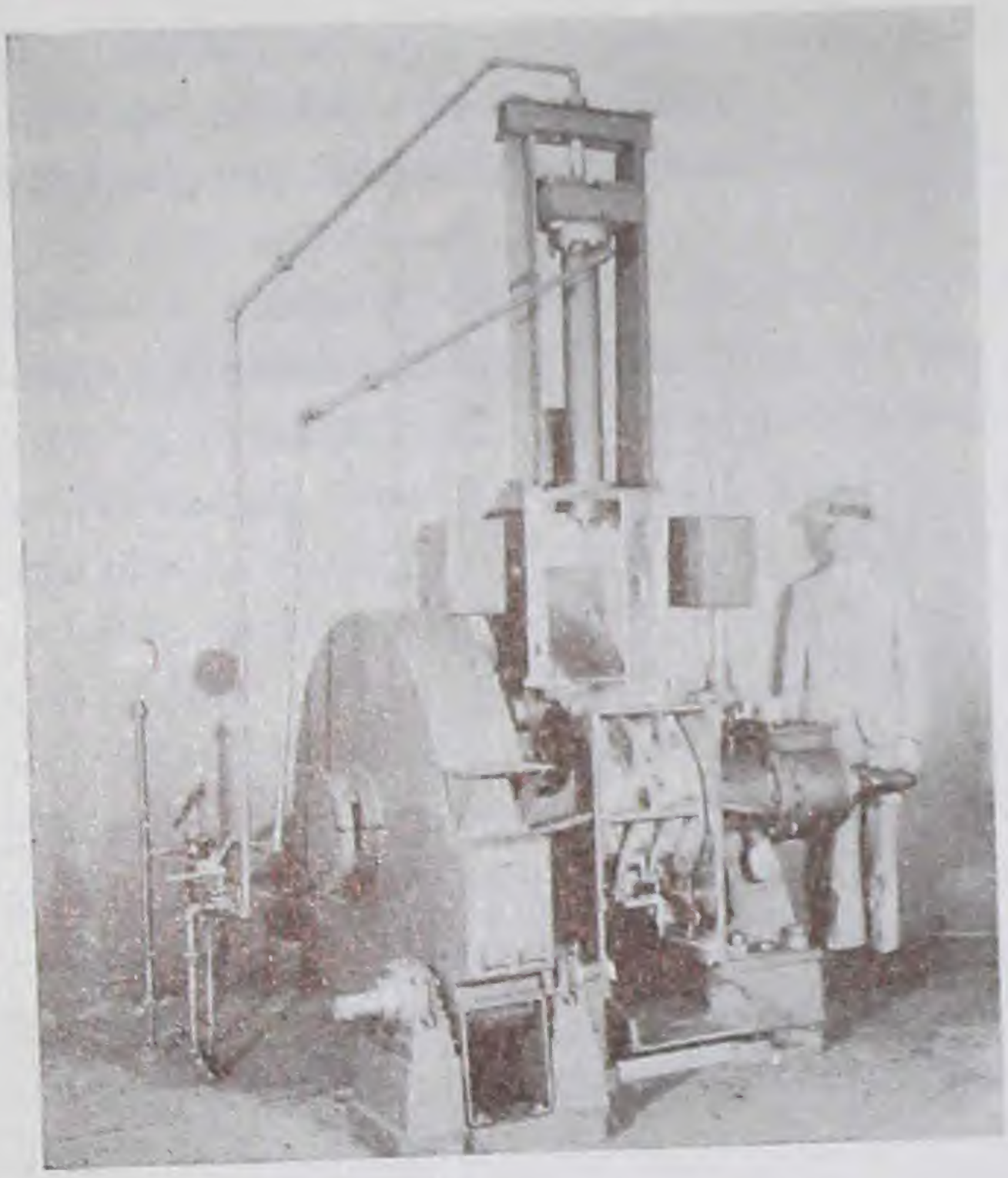


Fig. 12—Positive mastication mixer of the Banbury type (Farrel-Birmingham Co.)

When the plasticizer and thermoplastic material have been thoroughly mixed, they are removed to filter presses for removing excess solvent as described in the section devoted to the preparation of cellulose derivative molding compositions. Equipments of this description are particularly useful for blending compositions that cannot be handled satisfactorily in dry blending machines such as ball or pebble mills, where a mechanical dispersion does not necessarily produce the intimate blending of a wet process.

Spray Mixing: Extruders and molders of thermoplastics, particularly of the vinyls, have found that compounding of plasticizers and resins can be conducted economically by spray mixing. In this method, the resin particles are superficially wetted on their surface by a predetermined amount of plasticizer. Final blending occurs, for example, in the mixing action of the screw within the extrusion machine. Considerable quantities of vinyl plastic hose are produced in this manner.

Chapter III

Effects of Fillers Upon the Properties of Molded Plastics

Fillers play an important role in determining the properties of the thermosetting plastic molding compositions. Not only do they influence the method of handling the material during the molding operation, but they also affect the physical properties of the molded parts. This fact is highly significant to engineering design problems, for it means that special properties can be developed through the choice of appropriate fillers. It is common practice to designate a phenolic molding composition by its filler as, for example, wood-flour-filled phenolic, or asbestos-filled phenolic. In this manner the designer emphasizes those characteristics which are most important to his design.

The low-cost cellulosic fillers of wood or nut shell origin are among the most popular; and good, average mechanical characteristics are possessed by the molded parts. Without fillers of this nature, the mold shrinkage of thermosetting plastics would be excessive. While the nature of the filler, whether it be metal turnings or wood flour, does not affect tensile properties appreciably, qualities such as impact strength are profoundly affected. In general, the longer the filler, the higher the impact strength of the molded plastic.

Fillers are quite important to a number of moldable compositions prepared from natural resins such as shellac, though for the great majority of thermoplastic synthetic resins, property control is exercised through proper balancing of plasticizer content with the resin or through control of the molecular weight distribution.

In articles such as asbestos friction-brake blocks, powdered iron cores for telephonic equipment, or grinding wheel abrasives, synthetic resins or cellulose derivatives play less obvious roles as bonding agents. In general, it is the intent in such applications to employ just sufficient plastic to hold the fillers firmly together. In these as well as other examples of high ratio of fillers to resins, good flow during molding and high tensile strength are not at-

tained when complete resin continuity is lost throughout the structure because of high percentage of fillers.

From a fundamental scientific viewpoint, the effect of fillers on the properties of molded plastics will depend upon their size, porosity, distribution, purity, method of preparation, surface characteristics, and their chemical effects upon the resin. These characteristics are analyzed by the materials manufacturers who study fillers in the light of ease of compounding, molding, and final properties. In the discussions to follow, the origin, preparation, and characteristics of a number of fillers will be reviewed, and significant engineering applications cited.

TABLE X

Classification of Fillers

Organic Origin	Inorganic Origin
CELLULOSIC	MINERAL FILLERS
Wood flour	Asbestos
Cotton	Powdered mica
Alpha-cellulose	Silicates, clays, kieselguhr, talc
Paper pulp	Barytes
Shredded textiles	Whiting
Bagasse, corn husks, seed hulls etc.	Pumice, emery
Soya-bean meal	Zinc oxide, lead oxide, lime
Sisal	Calcium sulphide, barium sulphide
Cottonseed hulls	POWDERED METALS
Coconut shells	Iron
Walnutshell	Lead
Tirecord	Copper
CARBONACEOUS	Aluminum
Graphite	
Carbon black	
MISCELLANEOUS	
Powdered rubber	
Plasticizers	

The important phenolic plastics are classified in ASTM D-700 in accordance with the various fillers employed in their manufacture. The standard ASTM types are listed as follows:

Type 1—Unfilled, transparent or translucent for electrical and mechanical applications

Type 2—General-purpose, wood-flour-filled for electrical and mechanical applications

Type 3—General-purpose material with wood flour or cotton flock. Somewhat higher in impact strength than Type 2

Type 4—Moderate impact strength material with cotton rag or equivalent

Type 5—Medium impact strength material with cotton rag or equivalent

Type 6—High impact strength material with cotton rag, shredded fabric, or equivalent

Type 7—Electrical high-frequency, low-loss material with mineral filler
Type 8—Superior electrical high-frequency, low-loss material with a mineral filler
Type 9—General-purpose, mineral-filled for mechanical and electrical applications
Type 10—Heat-resistant, mineral-filled material.

Classification of Fillers

Fillers for molded organic plastics may be divided into two groups: Organic and inorganic. Many serve to improve the physical properties and are looked upon as reinforcing fillers. Others have no influence on the physical properties but, nevertheless, perform useful functions. For example, they may improve electrical and chemical properties, ease of compounding, or reduce cost. They are sometimes referred to as inert fillers and usually are inorganic in origin. Typical are powdered mica, slate flour, barytes, and whiting. It is difficult to recognize the fillers by a visual inspection of the molded product, unless the resin is present merely as a bonding agent such as in an abrasive grinding wheel. The various fillers used are classified in accordance with their origin.

In the following paragraphs some of the more important fillers for thermosetting compositions are reviewed. The specific utility of each filler and its properties are emphasized.

Wood Flour: One of the first fillers used in molding compositions and the most widely used filler today is wood flour. It serves to reduce the cost of the molded article, because its low molded specific gravity permits the attainment of a greater volume of molded parts per pound of molding material. When compared with inorganic fillers high in specific gravity, cellulosic fillers have a marked advantage on a volume basis.

In the preparation of wood flour, sawdust and shavings sometimes are employed as raw materials. In recent years, greater care has been exercised in the selection, origin and preparation of the woods. Soft woods from pine, Norway fir, spruce, and poplar trees, as well as hard woods from birch, maple, and oak trees serve as raw materials. Impurities such as bark or knots are eliminated, while a control is exercised over the color, natural gum content, residual moisture, and mesh size of particles. Although the size of the particles may vary considerably, the mesh

size of wood flour employed in molding compositions is about 100. The significance of grinding and pulverizing the batches of wood in different mills has been brought out by some investigators.* For example, it has been pointed out that attrition grinding of wood flour, in which the fibrous nature of the particles is affected so that a random distribution of fibers rather than preferred alignment is produced, tends to give higher strength to molded articles.

In general, a thorough blending of the wood flour and resin is resisted when the cellulosic fibers tend to knit together in a closely aligned group, and also when a high proportion of the natural gum content and lignin are present. Other factors also influence the preparation of wood flour compositions. Optimum mesh size of particles is determined from a number of factors. They include ease of compounding, preforming properties, molding qualities, and appearance of the finished molded article. For good electrical properties, low moisture content in the wood flour is desirable. To obtain these properties, carefully graded wood flour is oven-dried to remove excess moisture and stored in air-tight drums until ready for compounding.

As a general purpose material, wood flour enhances a number of properties of the molded piece, establishing a fair compromise among the various factors. Fair shock resistance, excellent appearance, good molding, high-tensile strength, good electrical properties, and low thermal conductivity are some of the characteristics displayed by wood-flour-filled phenolic compositions. Many applications of wood-flour-filled phenolic compositions reflect these characteristics. For example, the telephone housing in *Fig.* 13 illustrates a well-known application of wood-flour-filled phenolic compositions. High-gloss surface, reflecting a well-polished mold, good flow properties, and good dimensional accuracy are displayed. Electrical applications also are many, typical of which is the ignition distributor housing in automobile systems. Units of this description have been molded of phenolics for a number of years. More recently mineral-filled urea or melamine plastics have proved more satisfactory for aircraft ignition housings at high altitudes because of superior arc resistance.

Temperature limitations are imposed upon phenolic molded

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*"Filler Requirements", V. Meharg—*Modern Plastics*—Oct. 16, 150, Oct. 1938.

TABLE XI

Molded Plastics and Relation of Fillers to Applications

Resin Binder	Nature of Filler	Characteristics Displayed	Typical Examples
Phenol formaldehyde	Wood flour	General characteristics	Housings for radios, closures for bottles, misc.
Melamine formaldehyde	Mineral	Good arc resistance	Ignition distributor housings
Urea formaldehyde	Purified wood cellulose	Appearance—translucent	Housings for clocks, handles
Phenol formaldehyde	Cotton fibers	Improved impact resistance, good surface appearance	Telephone handsets, handles for surgical instruments
Phenol formaldehyde	Shredded fabric	High impact strength	Housings for drilling and grinding machines, small gears, couplings, mechanical governors
Phenol formaldehyde	Graphite	Lubricating qualities	Small, lightly loaded, self-lubricating bearings
Phenol formaldehyde	Asbestos	Heat and chemical resistance	Brake lining, clutch facings, plugs, and receptacle bodies for heating appliances
Phenol formaldehyde	Mica	Low-loss electrical properties	Coil housings, mechanical supports for radio parts

parts employing woodflour fillers. Continuous operation above 250-275 F is infrequent because of the permanent reduction in physical properties due to deterioration of the cellulose. However, the low thermal conductivity is advantageous to oven control knobs. Impact strength of woodflour-filled compositions is only moderate and if high impact is required some cotton or fabric fillers are included. If improved heat resistance is desired some mineral

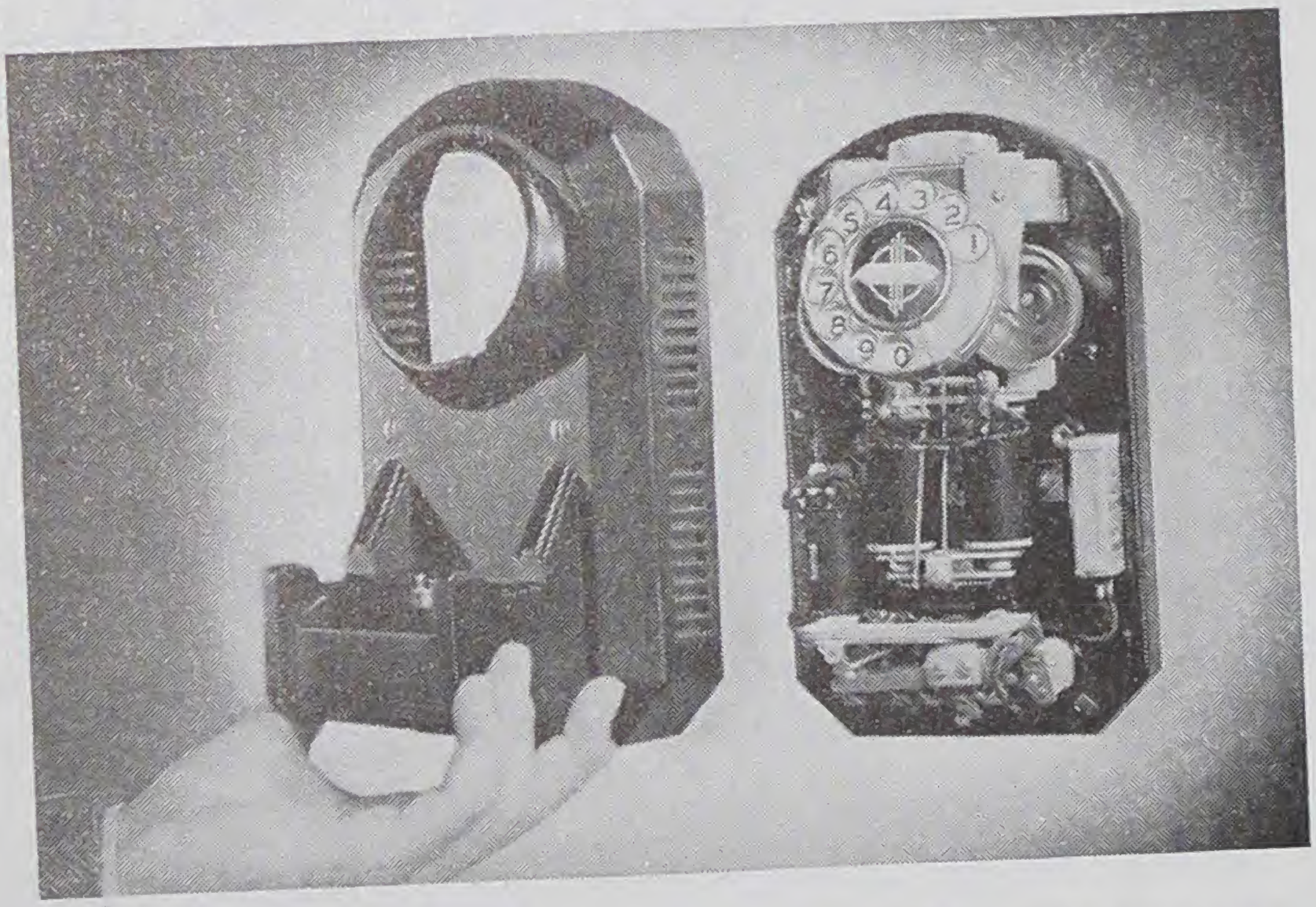


Fig. 13—Housings formed in steel dies under hydraulic pressure

fillers may be included with the woodflour. TABLE XI illustrates the influence of application upon the type of molding compound, as determined by its filler.

There has been considerable interest from time to time in the possibility of molding sawdust. The properties of such moldings are usually quite inferior unless large amounts of synthetic resin are employed. Some improvements appear to be forthcoming, however, by prior coating of the fillers with a rubber or non-penetrating resin film, so that it is adsorbed on the surface rather than into the filler. Dry blending of fillers and resin also achieve this optimum relation.

Alpha-Cellulose: Purified wood cellulose of a light bleached pulp is used in urea formaldehyde molding compositions. The alpha cellulose is sheeted and introduced into the blending tank with an early stage of the urea-formaldehyde resin. Inasmuch as

the urea plastics are characteristically translucent, the filler must be clean and free from all impurities. Thorough wetting and penetration of the alpha-cellulose fillers by the urea resin promotes translucency and permits attainment of many light shades and colors. Many of the desirable physical properties of urea plastics are rendered permanent by the addition of alpha-cellulose, which vastly improves the utility of these materials. While ordinary wood flour has been used in lieu of alpha-cellulose in urea-plastic compositions, it is suited only to the darker shades of color. It is, however, less expensive than the alpha-cellulose.

Cotton Fillers: Cotton fillers are introduced into molding compositions to improve impact qualities, though not to the same extent as shredded textiles. However, surface appearance is maintained and desirable physical properties are transmitted to the molded parts. When the cotton filler is ground to a fine mesh size a fluffy product is formed, tending to clot and sometimes requiring screening prior to mixing with the resin. Cost of this cotton flock is appreciably more than wood flour, a factor which no doubt has been a deterrent to its more extensive use. Cheaper cotton linters sometimes are used as fillers, though they are not as free from impurities as the higher grade cotton flock.

Cotton fillers are also used in combination with other fillers to improve certain qualities, such as low dielectric loss, not obtained with cotton fillers alone. Powdered mica, on the other hand, receives mechanical benefit through the inclusion of cotton fillers. There is growing interest in oriented high-strength, cotton-fiber pads saturated with phenolic resins, which lend themselves to the production of sheets or molded parts. One manufacturer's product ("Avtex"), shows tensile strengths about double that of a wood-flour-filled molding composition.

Paper and Pulp: Paper and pulp products are destined to play increasingly prominent roles in the preparation of molding compositions. While ordinary shredded paper may well serve as a filler in molding compounds, interest of the molders and materials manufacturers goes beyond this. There are three distinct varieties which offer many possibilities:

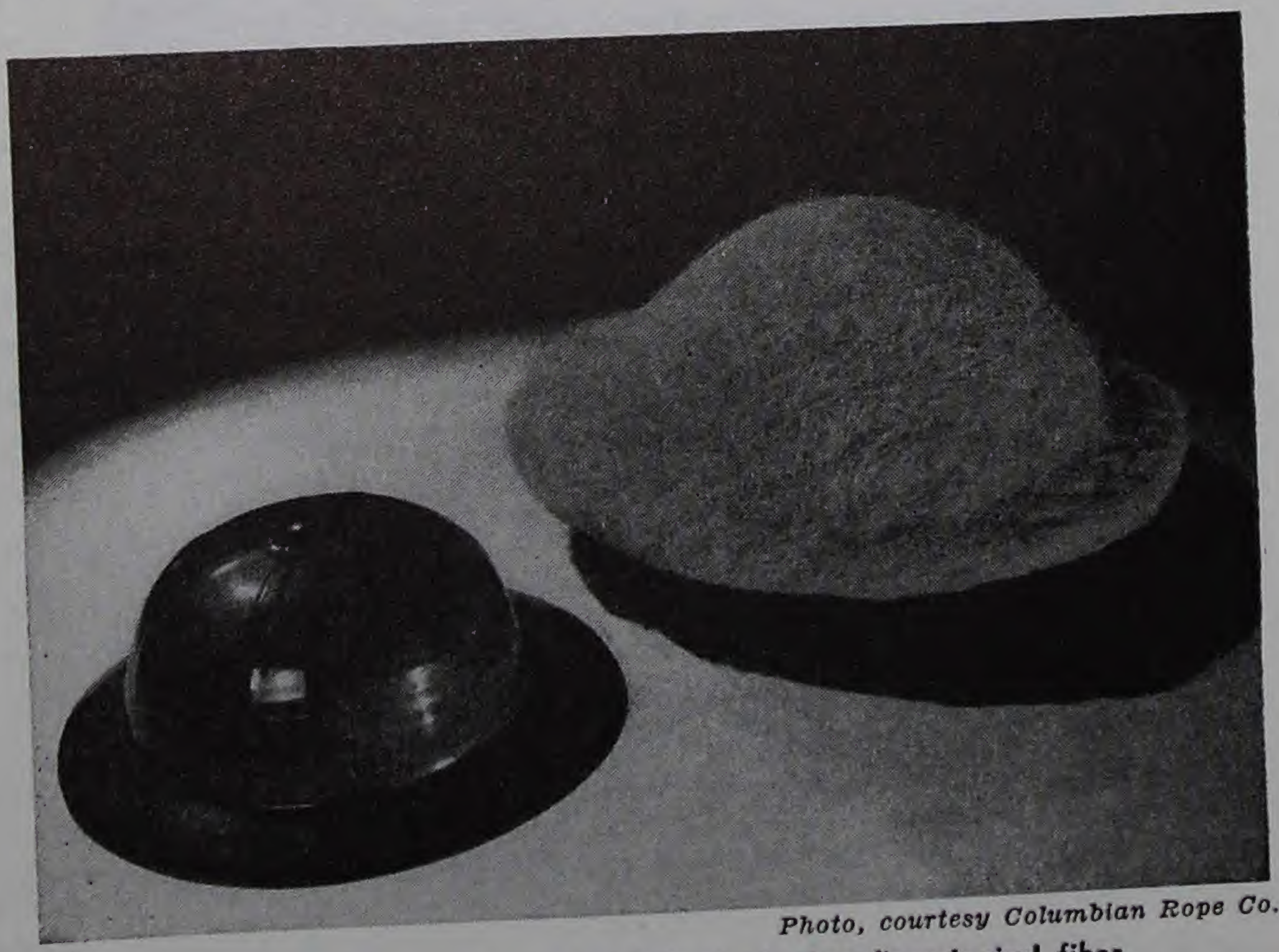
1. Lay-ups of resin and paper fibers to reinforce weak portions of molded articles (for example, "Rogers-board")
2. Resin-impregnated paper which previously has been creped to

assist flow during molding. This has been a useful product in molding thin-walled instrument cases and the like

3. Resin-impregnated pulp preforms with close interlacing of cellulosic fibers, laid up on a vacuum screen approximately shaped to the mold dimensions. For preparing molding compositions in the development of large, contoured surfaces, this technique undoubtedly will be fostered by the paper industry to be of service to plastics molders.

In the latter method, the predistribution of resin and reinforcing fillers greatly assists the molding operation. Final products show a remarkably high tensile strength—about double that of ordinary molded parts—when the resin impregnation is conducted in the wet slurry before the paper fibers are given final shape on the vacuum screen.

Sisal Fibers: Also in fulfillment of the demand for preforms containing a predistribution of fibers and resin, phenolic-resin-sisal pads have been featured in numerous articles, such as molded droppable fuel tanks and helmets (*Fig.* 14). A batting of sisal



Photo, courtesy Columbian Rope Co.

Fig. 14—Preform and molded helmet of phenolic-resin-sisal fiber

fibers is immersed in a phenolic resin solution, squeezed of excess resin, and sold as resin impregnated pads ("Corolite").

Shredded Textile Products: Inclusion of shredded textile products in molded plastics, has been one important factor in promoting the application of plastics to machines. Parts molded with fabric filler display considerably greater impact strength than that manifested by other molded materials. An increase in impact strength of as much as ten times over the wood-flour-filled plastics has been noted for fabric-filled molded parts. The shredded textile fillers include miscellaneous textile clippings, shearings, and scrap. The added strength of the molded piece is due not only to the strength of the fiber but also to the spinning, weaving, or cross-locking of the fibers. In effect, molded plastics with shredded-fabric fillers, represent an intermediary stage between wood-flour molded plastics and laminated canvas-base plastics, with respect to impact strength and general physical properties. There are, however, certain disadvantages accruing from the use of molded plastics with shredded-fabric filler, often overlooked for mechanical properties.

1. Surface finish is mottled with the heterogeneous patterns of the fabric filler, lacking smooth, uniform texture of other fillers, such as wood flour. In the case of equipment such as oil drilling machinery, where large fabric-filled moldings, weighing several pounds, are widely used and subject to much abuse, appearance is of little concern. Fulfillment of the mechanical and chemical requirements are paramount in these examples, which are served by no better material than fabric-filled phenolic plastic.

2. If the part molded with shredded fabric requires further finishing operations, such as sanding or grinding to size, a smoothly trimmed edge is not easily obtained. The resin content may be machined, but strands of fiber clinging tenaciously to the body of the material may leave a coarse finish on the machined edge.

3. A final disadvantage of shredded-fabric-filled molded pieces is that they may not be preformed as readily as other molded products, prior to molding, and slow down the molding cycle.

In spite of the limitations of shredded-fabric-filled phenolics, notably those which necessitate bulky molds due to difficulty in preforming the powder automatically, there is increasing demand for this material in engineering designs, by reason of its high impact strength. Among the designs which have employed this material are small molded gears and couplings, lightweight port-

able machine housings, aircraft control cable pulleys, rayon spinning buckets and many others. A molded heavy-duty fishing reel of impact-resisting phenolic is shown in *Fig.* 15. Many of the molded parts manufactured for the armed services in World War II were molded of impact-resisting phenolics, which offered good serviceability under much mechanical abuse.

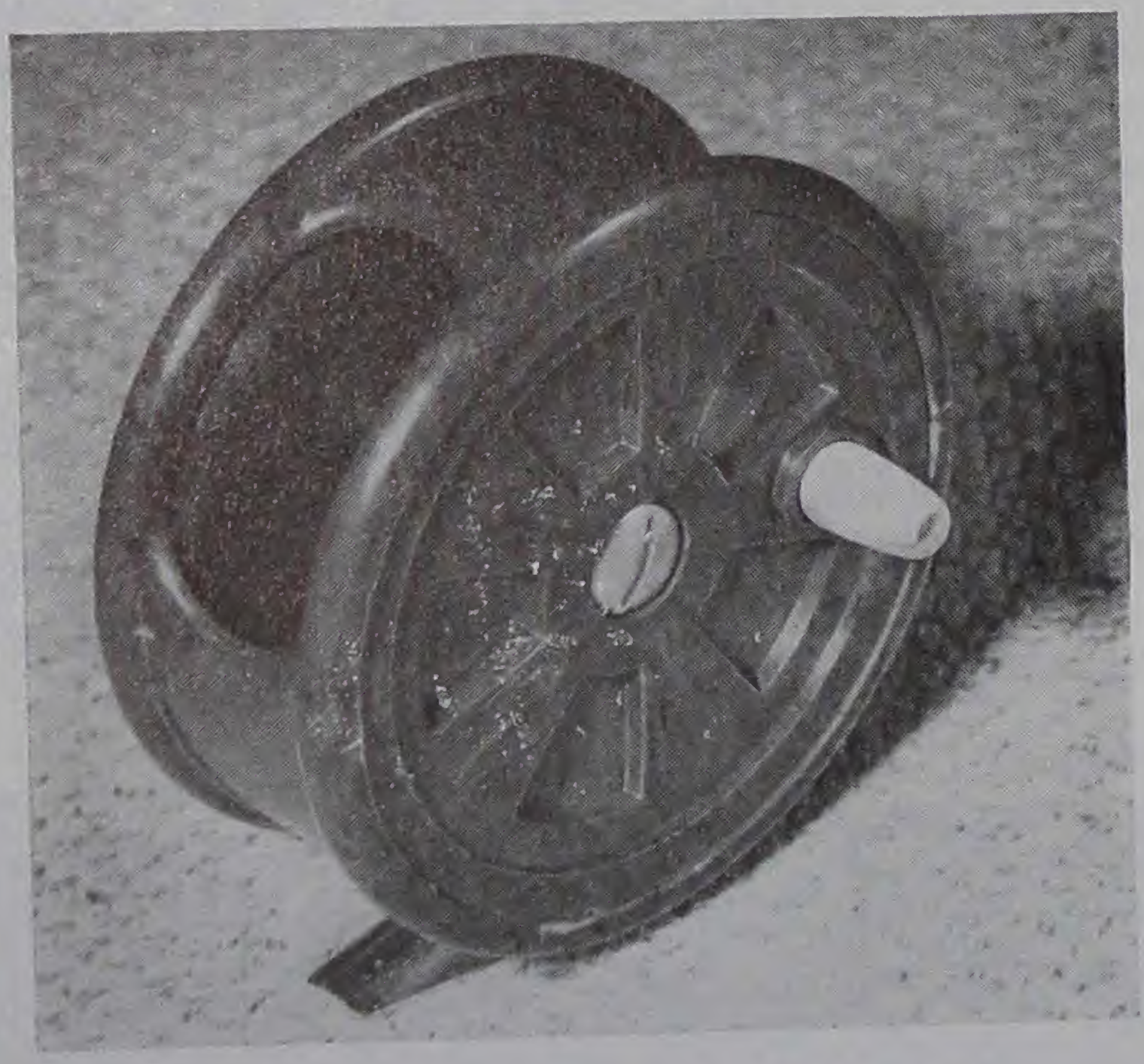


Fig. 15—Impact-resisting molded fishing reel

Tire-Cord Filler: Offering impact strength even higher than that of the shredded-fabric-filled variety, tire-cord-filled moldable phenolics fulfill maximum impact requirements. While handling the tire-cord-filled material during molding entails additional problems, the mechanical advantages of the final product offset these factors. The material was developed for the same types of applications as the shredded-fabric-filled variety.

Miscellaneous Organic Fillers: Many attempts have been made to find substitutes for the organic fillers, notably for shredded-fabric materials. The substitutes either failed to exhibit equally satisfactory properties or were too high in cost. Jute, kapok, hemp, and flax often are mentioned as possibilities though high moisture absorption in some cases places restrictions on the

material. Other vegetable fibers also are the subject of investigation although none are outstanding as yet. While various molded compositions have appeared in which the natural binder content is used rather than the synthetic resin, they lack the mechanical properties of synthetic plastics.

Other organic fillers of note are powdered cork and powdered rubber; the former tends to decrease the specific gravity of molded pieces, and the latter increases the coefficient of friction on the rubbing surface.

Graphite and Carbon Black: Carbon black does not have the same significance to synthetic resin compositions as it has to natural rubber, where it permits the attainment of superior physical properties. It is useful, however, for its high screening power in small quantities, though a minimum is used in molded compositions intended for electrical applications. Nevertheless, special grades of carbon and graphite are employed in the manufacture of resin-bonded resistors and commutator brushes for electrical purposes, where a high proportion of filler content prevails. The resistance to the passage of electrical currents is determined in part by the carbon-to-resin ratio and the compressive pressure employed. Graphite is desirable for its self-lubricating qualities also. It often is added to molding compositions as a lubricant during the molding operations. More often, however, it is applied to act as a lubricant for small, self-lubricating bearings. Under large loads and high speeds the self-lubricating properties are nullified by the poor heat conductivity of the bearing material. Other applications use graphitic fillers because of their acid-resisting properties.

Other forms of carbon black can bring out special qualities in the plastics. In this connection the role of acetylene black may be observed. The writer has observed that the addition of about 10 per cent acetylene black will render the molding compositions electrically conductive, a factor which has proved most useful in preheating molding materials by low-frequency resistance methods.

Asbestos: Molding and casting resins find in asbestos a filler which will reduce mold shrinkage to about one-half that realized with other fillers. Asbestos is the most widely used mineral filler for molded plastics. It is an inorganic material, sometimes referred to as rock wool, and there are several grades known to

the plastics trades, all purporting to fulfill a number of desirable properties. Fine fiber asbestos, known as "floats", is applied widely in molding compositions requiring resistance to chemicals and high temperatures. Asbestos is a splendid heat insulation and enables molded parts to withstand temperatures considerably in excess of that normally allowed by the resin content, though the actual thermal conductivity of asbestos-filled plastics is higher than wood-filled plastics. Though the shorter and finer grades of asbestos will give a better surface finish, they will not impart as high an impact strength to the piece as will the larger asbestos fibers. To retain full strength, the easily broken asbestos fibers are handled carefully at the time of resin impregnation, to insure full coverage of the large fibers. The long fibers are preferably blended to the resin without rolling or grinding, by employing a resin varnish for impregnating. Special precautions must be maintained during the molding operations to insure the proper filling of the mold cavities. Shorter asbestos fibers are incorporated in molding compositions by the conventional dry processes, in suitable mills.

Mineral asbestos is superior to wood flour in its general resistance to chemicals and moisture. These characteristics are displayed to best advantage in miscellaneous chemical apparatus and accessories. Small towers and chemical storage tanks have been made of a special phenolic-asbestos composition, resisting most acids and alkalies, except strong oxidizing acids. In some applications, resin-impregnated asbestos has been applied direct on metal surfaces. For good electrical properties, asbestos must be purified so as not to affect dielectric qualities.

Heat-resisting applications of molded asbestos-filled phenolic plastics are numerous and include electrical switch insulation, ash trays, cord connectors, plugs, housings for heating units, etc. However, the hot-molded compositions do not possess the best electrical properties and are not arc-resistant. The high specific gravity of molded asbestos-filled phenolics increases the cost appreciably, though no suitable substitute has been found which will combine heat resistance with strength. Asbestos-filled, cold-molded compositions of bitumen or synthetic resin binder are well known, and possess many desirable qualities, though a low tensile strength. However, arc resistance is improved, and retention of strength after prolonged exposure to high tempera-

tures is also a factor in their favor. Other applications include brake linings and clutch faces in which a high proportion of filler to resin is present, where the resin acts more in the capacity of a binding agent for the asbestos.

Mica: As an insulating material, both at high and low temperatures, mica has few rivals. Chemically, mica is a complex form of an aluminum silicate and potassium or magnesium silicate. Various commercial grades are available that are stained, spotted, or clear. In molding compositions the mica splints are ground up to a fine mesh size, just like any other filler, and introduced into the molding composition. It may be necessary to add some fibrous filler as a reinforcing material as mica-filled phenolics tend to be brittle. Powdered mica phenolics constitute a group of highly desirable materials, known as low-loss materials, and exhibit superior insulating properties particularly at radio frequencies.

Laminated mica sheet is formed of mica splints, bonded together by an alkyd or phenolic resin. The proportion of filler to resin is high in these instances. Among the applications of molded mica-filled phenolics are those to coil forms, condenser housings, terminal blocks, etc., of wireless equipment where low dielectric loss is imperative if the phenolic material is to compete with molded inorganic refractory compositions. Low moisture absorption is another advantage in favor of the plastic material.

Abrasives: While abrasives are not employed as fillers in hot molding compositions, they may be mentioned in connection with abrasive grinding wheels and papers in which a synthetic resin is employed as a bond. Phenolic-resin-bonded abrasive wheels employing aluminum oxide as an abrasive are widely used as cut-off disks for metal stocks. Approximately 90 per cent of abrasive to 10 per cent of resin, by weight, is present in these compositions. Synthetic-resin-bonded silicon carbide also is currently used on an important grade of flexible abrasive belts, permitting operations in wet or dry media which proved detrimental to glue bonding.

Diatomaceous Silica: Another example of an inorganic filler for molded phenolics is diatomaceous silica, obtained from fossil marine deposits of microscopic plants. It has a comparatively low specific gravity, offering certain advantages in price per pound. Advantages accruing from the use of this filler and other inor-

ganic materials of a similar nature are an increase in surface hardness, lower cost per pound of molding material, improved electrical properties, and lower water absorption. These advantages are offset somewhat by increased brittleness. Battery cases and battery plate separators have been molded with this material present as a filler, contributing to improved chemical resistance.

Barytes: Barytes or barium sulphate fillers are well known in synthetic resin molding compositions by reason of their inertness and resistance to various acids. A specially prepared material, blanc-fixe, obtained in a white powdered form by treating barium salts with sulphuric acid, also is used in compounding. The barytes are used also in the preparation of cold-molded compositions, lowering the cost and improving the resistance to high temperatures. They serve to fill voids between asbestos fillers, thus yielding a denser article.

Whiting: Whiting, obtained by grinding limestone (calcium carbonate) is widely used in rubber compounding, though considerable use is found for it in phenolic compositions. Cold molded phenolics use whiting in conjunction with asbestos as fillers for many compositions, the whiting permeating the fibrous structure of the asbestos.

Miscellaneous Inorganic Fillers: Types of inorganic mineral fillers that have been applied to molded plastics are so diversified, and cover such a broad field of application that it would serve little purpose to attempt to discuss the characteristics of each. Rather a few general remarks will be made, pointing out the analytical reasons governing their selection. Cost of fillers and their specific gravity are important considerations, inasmuch as fillers with high molded specific gravity will not give the same volume of molded products as an equivalent weight of molding composition with low specific gravity fillers. This places at a disadvantage some fillers such as zinc oxide and lithopone, which have high specific gravities (5.6 and 4.1).

Often inorganic fillers are added to develop certain properties which the resin or organic fillers do not inherently possess. Hardness and inertness to chemical attack are two prime reasons for the widespread use of inorganic fillers. There are other properties such as lubricating qualities where fillers like powdered talc and sericite prove useful. Another example is the development of luminescent qualities in molding materials, chiefly

through the use of specially prepared calcium sulphide. It might be mentioned that greater success has been encountered with the addition of these fluorescent inorganic fillers to thermoplastics than to other compositions. Several promising fluorescent molding materials are now in development which will find wide use in the home and on automobile accessories.

Summarizing, it is possible to list those qualities of organic and inorganic fillers which make them useful additions to molding compositions. While no one filler possesses all of the properties tabulated below, some exhibit various combinations:

1. Low cost and large supply of raw materials
2. Low specific gravity in the molded form
3. Ease of compounding into molding compositions
4. Purity and absence of unsuitable impurities
5. Ease of grinding and preparation for introduction into compositions
6. Inert to chemical attack and their effect on other ingredients of molding composition and the mold steel
7. Improvement in molding qualities, and preforming qualities
8. Improvement in physical properties, notably impact strength
9. Improvement in electrical properties
10. Improvement in behavior toward heat
11. Reduced shrinkage of molded parts.

Metal Fillers: The growing importance of metal powders for industrial purposes warrants special attention. While many powder-metal products are prepared at high temperatures and under high pressures without the benefit of organic plastic binders, there are certain applications which benefit from the addition of an insulating medium as a binder for the metal powders. In developments of this nature, the proportion of resin to metal-powder filler is low, and the article is preponderantly metallic in nature. Practically every well-known commercially used metal is now available in powder form of different mesh sizes. In general, the synthetic-resin-bonded metallic powders have tended to be brittle in the absence of a fibrous filler unless some metallic wool is present, though at the same time thermal conductivity is much improved. Adverse effects, of course, accrue from susceptibility of metals to chemical attack. A discussion of some of the better known resin-bonded metal powders follows:

1. POWDERED IRON: In certain electrical apparatus cores

molded from iron powder possess unique electrical properties at radio frequencies and permit the development of smaller coils with less copper. Exhibiting a permeability as high as 4, space requirements are reduced, and at the same time the figure of merit of the coil (ratio of inductance to resistance) is increased. Damaging eddy currents are kept to a minimum inasmuch as the iron is in a finely divided form and separated by a synthetic resin with good insulating properties. Phenolics, polystyrenes, and urea plastics have been mentioned as various binders for powdered cores of this description and have been reviewed in detail.* The iron powder may be prepared by electrolytic methods, reduction from the oxide, thermal decomposition of the carbonyl, or from scrap stock in rolling or grinding operations. The small spheres produced from iron carbonyl offer minimum internal friction during molding.

2. POWDERED LEAD: Yielding a molded product with a high specific gravity, lead powder has been of some utility to phenolic molding compositions. It has found limited applications as a bearing material, where the self-lubricating qualities of lead were deemed desirable. In developing a composition for a bearing, a balance must be reached whereby physical properties such as impact resistance are not too adversely affected by high metal content. At the same time the lead particles must not be too thoroughly covered by the resin, otherwise lubricating qualities of the lead will be lost.

A rather important application of powdered lead and phenolic resin binders made its appearance in 1945, when the T-44 frangible bullet was developed for the training of aircraft gunners. Comprised of 90 per cent lead and 10 per cent phenolic resin, the bullets were transfer molded with approximately 80-second cure cycle. On striking the target airplane they would disintegrate, leaving a tell-tale mark to record the hit. With a specific gravity above 5.0, they could be handled in standard machine gun equipments.

3. POWDERED ALUMINUM AND POWDERED COPPER: Possessing unusual decorative value, powdered aluminum has been used in thermoplastic molding compositions. The powders are flakes, .00001 to .00007-inch thick, oriented at random throughout cellu-

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*"Metal Powders and Plastic Binders", J. Delmonte, *Modern Plastics*—Page 49, May, 1939.

lose plastic compositions. Light rays are reflected from the surface in every direction giving a sparkling effect. A thin film covers the outside, preventing tarnishing or change in reflecting qualities. The powders that are employed in these compositions are referred to as "lining powders". They are produced under repeated blows, such as stamping, in which the particles not only are reduced to a flake-like form but also retain the metallic luster by the burnishing action. Also of note are cellulose plastic compositions employing scrap turnings of brass, steel, or aluminum for decorative purposes.

Metal-graphitic grades of resin-bonded motor brushes have employed relatively large proportions of powdered copper. The copper serves to reduce the brush electrical resistance, yielding a commutator brush suited to low-voltage machines, such as electroplating generators, where a minimum brush drop is imperative. Phenolic and alkyd resins have been used as binders for such brush compositions.

With this brief review of metallic powders as fillers, the significance of fillers as an alloying agent for numerous plastics is emphasized again. While actual chemical combination does not take place between the filler and resin, a physical combination ensues which serves to develop desirable properties of both materials. Thus it is seen that control over the nature and quality of the resin, as well as the filler content, permits the development of many materials useful for engineering purposes.

Chapter IV

Physical Properties of Plastic Materials

Organic plastics in cast, laminated or molded form are engineering materials of construction. They may compete with or supplement existing designs in wood, and ferrous or nonferrous alloys. In this chapter, the physical properties of the plastics are examined and in some instances compared with other materials. This examination will not only report values determined by ASTM standards, which are universally employed by the major materials manufacturers, but will also include sufficient data to enable engineers and designers to determine the performance of the plastics at temperature extremes. Plastics are basically temperature-sensitive materials, differing only in the degree to which they exhibit this temperature sensitivity. They have been formulated to be molded or laminated under heat and pressure, and in their final form manifest variation of properties with temperature.

The physical properties of most plastics change not only with temperature, but in some instances with variations in moisture content. To understand the plastics, one must also examine their behavior in weather exposure, under changing humidities and in the presence of sunlight. Water already has been identified as a plasticizing agent for proteins, and its removal would lead to embrittlement of these materials. Not all plastics, however, have their physical properties dependent upon humidity, because some of the materials are quite impervious. In general, the effect of chemicals or solvents upon plastics can be followed through a change in some physical characteristic.

The designer employing plastics materials must not only apply engineering data to plastics in the correct manner, he must also interpret these results in the light of manufacturing methods. For example, the fact that a certain molding compound is rated with a tensile strength of 7000 psi is no assurance that this value will be reached by a given article unless careful and precise molding methods are followed. Insufficient cure in the material or the presence of flow marks may seriously detract from the quality of a plastic material. Final properties are closely dependent up-

on manufacturing methods and the properties of a plastic should be qualified by some reference to the method of production.

The range in physical properties emphasizes the versatility of plastics. Through compounding with various fillers and plasticizers, any degree of toughness or elongation may be obtained. It is important that test data be obtained by approved, accepted standard testing techniques if comparisons with other materials are to be effectively made. For this reason, applicable standard testing methods will be cited in the chapters on properties.

Specific Gravity

In the field of aircraft and in the design of portable machines, there is a marked advantage in the low specific gravity of plastics materials. While solid plastics can effect appreciable savings in weight in some circumstances, it is seldom that the material is selected on a weight basis alone, and other physical factors must be taken into consideration. In general, plastics average about one-sixth the weight of steel and one-half the weight of aluminum, though about twice the weight of the more common species of wood. Of the plastics, polyethylene possesses the lowest specific gravity (0.92) in solid bulk form. Comparative values are listed in TABLE XII.

Specific gravity of the plastic materials is dependent not only upon the resinous binder, and its fillers or plasticizers, but also upon the method of manufacture. In the preceding chapter on fillers it was pointed out that specific gravities as high as 5.0 were obtained with powdered lead fillers in special molding compounds for aircraft gunnery practice bullets. The other extreme appears in the manufacture of low-density, bubble-filled plastics which may have densities as low as 2 pounds per cubic foot. At the end of this chapter some of the physical properties of low-density plastics are tabulated. Plastics are indeed versatile materials, and densities may be adjusted during manufacture to fulfill specialized engineering requirements.

The molder of course, is fully cognizant of the differences in specific gravity of the molded plastics and if, for example, two competitive molding materials cost the same on a pound basis, selection of the lower-specific-gravity material is obvious, assuming equivalence in property values and molding qualities. Aside

from their low average specific gravities, plastics have another weight advantage over other materials of construction, in that a given mass of material may be molded or laminated easily into an efficient structural design embodying integral reinforcing ribs or stiffening members.

Tensile Properties

In their broadest physical classification, plastics may be described as rigid and nonrigid materials. This distinction is purely arbitrary and based upon the relative amounts of elongation. The stiff, rigid types do not usually have more than several per cent elongation below the elastic limit, though the nonrigid varieties may stretch more than 100 per cent. The nonrigid plastics, sometimes referred to as elastomers, find their greatest usefulness as a rubber substitute, combining good chemical resistance with low-temperature flexibility in a number of important

TABLE XII

Specific Gravities and Weights of Plastics

Plastic Material	Description	Specific Gravity	Weight (lb/cu/in.)	Specific Weight (cu/in/lb)
Phenol formaldehyde				
Molded	Cast resin	1.27-1.32	.046 -.047	21.8-21.0
Molded	Wood-flour filler	1.34-1.52	.0485-.055	20.6-18.2
Molded	Fabric filler	1.37-1.40	.0496-.0506	20.2-19.8
Laminated	Asbestos filler	1.70-2.09	.0615-.0756	16.3-13.2
Laminated	Paper base	1.34-1.55	.0485-.0561	20.7-17.7
Laminated	Fabric base	1.34-1.55	.0485-.0561	20.7-17.7
	Asbestos paper base	1.60-1.65	.0579-.0597	17.3-16.8
	Alpha cellulose	1.48-1.50	.0535-.0542	18.7-18.4
Urea formaldehyde (molded)	Molded	1.05-1.07	.038 -.0387	26.3-25.8
Polystyrene	Molded	1.38	.050	20.0
Polydichlorostyrene	Unfilled plastic	1.34-1.36	.0485-.0492	20.6-20.3
Polyvinyl chloride acetate	Sheet	1.27-1.37	.0460-.0496	21.8-20.2
Cellulose acetate	Molded	1.27-1.63	.0460-.0590	21.8-17.0
Cellulose acetate	Molded	1.21	.0436	22.9
Cellulose acetate butyrate	Molded	1.19	.043	23.1
Cellulose propionate	Molded	1.1 -2.7	.040 -.0975	25.0-10.2
Shellac	Molded	1.14	.0412	24.3
Ethyl cellulose	Sheet	1.18	.0427	23.4
Methyl methacrylate	Molded	1.35-1.60	.0488-.0578	20.5-17.3
Cellulose nitrate	Sheet	1.33	.0481	20.8
Casein plastic	Pure resin	1.32	.0483	20.9
Allyl type	Cast	1.4	.0506	19.8
Polyvinyl chloride	Pure resin	1.6 -1.75	.0578-.0633	15.8-17.3
Polyvinylidene chloride	Filament	2.1	.076	13.1
Polytetrafluoroethylene	Sheet	1.08	.0391	25.5
Cumarone-Indene	Pure resin	1.19	.043	23.1
Polyvinyl acetate	Pure resin	2.00	.072	13.9
Cold molded bitumen	Asbestos filler	1.14	.0412	24.3
Polyamide	Molded	.92	.0332	30.1
Polyethylene	Sheet	2.7	.0977	10.2
Aluminum		7.8	.282	3.42
Steel		1.15-1.25	.0416-.0452	24.0-22.1
Rubber, hard		2.3	.0832	12.0
Porcelain		.68	.0246	40.6
Maple		.86	.0311	32.2
Oak		3.0	.108	9.25
Asbestos		2.5	.0905	11.0
Glass plate				

industrial goods. On the other hand, the stiff, rigid type of plastic appears in cast, laminated, and molded products fulfilling numerous engineering functions.

The tensile strength of plastic materials is dependent upon numerous factors, including degree of polymerization, nature and distribution of fillers, proportions of plasticizers, temperature and humidity, and method of manufacture. Some of these factors are examined in more comprehensive detail in the following paragraphs.

Degree of Polymerization: It generally is recognized that the higher the degree of polymerization, the greater will be the tensile strength. As pointed out in Chapter II, the materials develop their tensile properties during resin formation and the establishment of strong primary bonds between molecules. After a resin converts from a liquid to a gel or semisolid state, it may be torn apart readily due to its low tensile properties. As the polymerization proceeds, tensile strength improves markedly to form a strong, rigid structure. An excellent study of this nature was made by Curme and Douglas*, who examined the property dependence of polyvinyl copolymers upon the average molecular weight. The gradual change in impact strength, modulus of elasticity, and tensile strength as a function of the degree of polymerization, as brought out in the curve of *Fig.* 16, may well be representative of similar thermoplastics. The tougher sheets of polyvinyl copolymers are obtained from the higher molecular weight compounds.

Variation of tensile properties with degree of polymerization is not limited to the synthetic resin, because recent investigations upon fractionated cellulose derivatives indicate the same dependence upon the degree of polymerization.** Also to be considered is the effect of side groups or substituents, which will produce a marked lowering of the tensile strength as they grow in size. For example, relationships have been established between the tensile strength of cellulose esters and the number of carbon atoms in the substituent groups forming the side chain. For synthetic resins, increased plasticity and lower tensile strength may develop with polymers formed from higher molecular weight monomers of a given series. This, for example, has been reported

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*G. Curme, S. Douglas—*Ind. & Eng. Chem.*—28, 1123, Oct. 1936.

**M. Harriss—*Ind. & Eng. Chem.*—37, 1945.

for the acrylics*, part of the data being tabulated in TABLE XIII.

Nature and Distribution of Fillers: When fillers are disconnected and randomly distributed, they do not have much bearing upon the ultimate tensile strength, though they do exert considerable influence upon impact, flexural strength, and creep. However, when they are present in proportions such that the cohesive

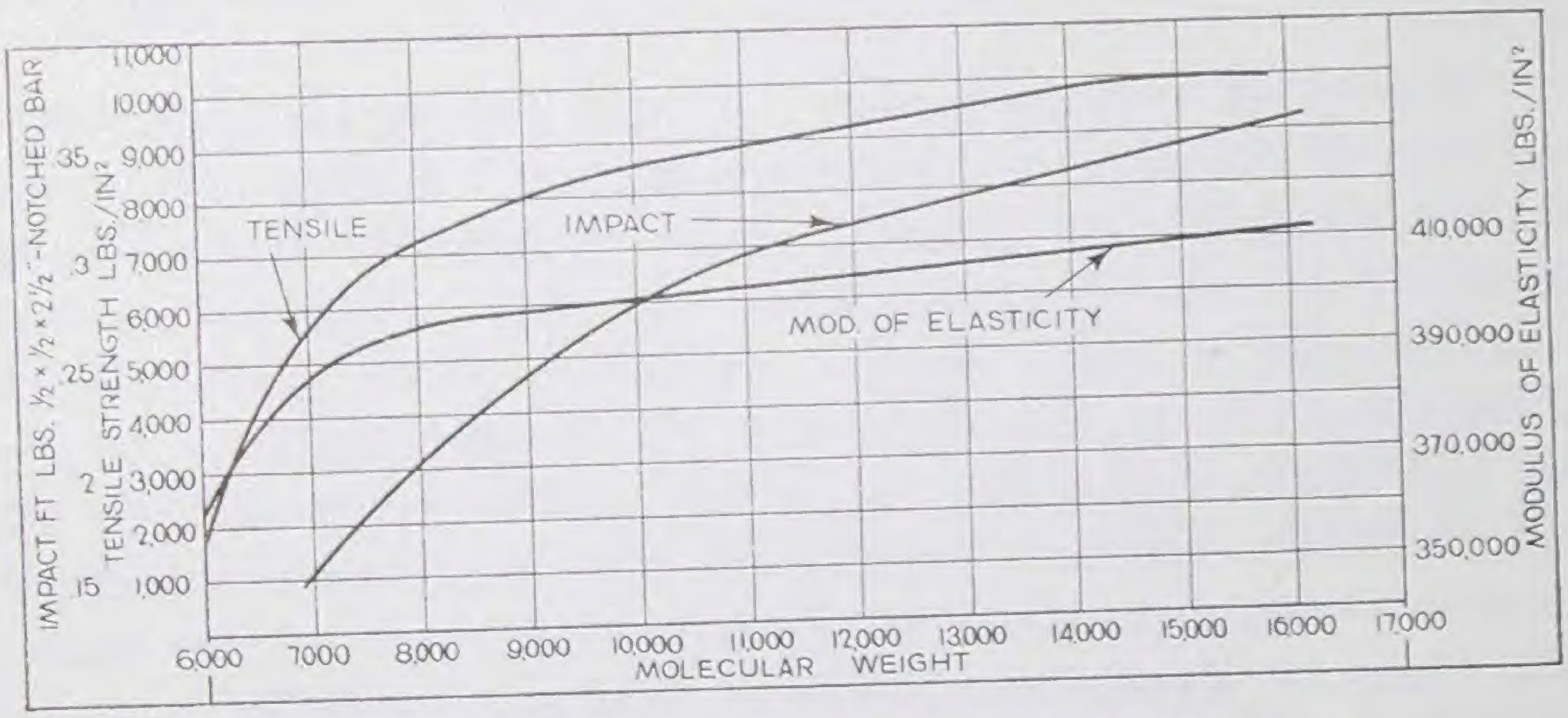

Fig. 16—Physical characteristics of polyvinyl chloride-acetate

forces betwen resin molecules are overshadowed by the adhesive forces between filler particles through the resin, the nature and identity of the fillers are important in determining tensile properties. In cold-molded compositions where there is little flow of the resin when molding under pressure, the tensile properties of the final substances are relatively low and are determined largely by fillers present. Closely interlaced fillers which may appear in resin pulp preforms, sisal fiber pads, or combed cotton or glass fibers, may yield molded or laminated products with superior tensile properties. It is known, for example, that the tensile strength of molded pulp fibers treated with phenolic resin is about twice that of ordinary wood-flour-filled phenolic compositions. This same principle is carried further in the manufacture of laminated products, where continuous filaments from a woven textile product will exert a major influence on tensile properties. Continuous in length and preferably under some initial tension, they are capable of absorbing some of the tensile load

*Dittmar, Strain and Kennelly—*Trans. Elec. Chem. Soc.*—Page 159, Oct., 1938

otherwise assumed by the binder. In one striking example, oriented glass fibers bonded into laminates with the aid of synthetic resins will exhibit tensile strength in excess of 100,000 psi. Special high-tenacity cellulosic fibers ("Fortisan") woven into textile products also contribute to the development of exceptionally high strength-weight ratios among the laminated products.

Proportions of Plasticizers: As already pointed out, plasticizers play an important role in the manufacture of certain thermoplastic materials, developing desirable flow properties during molding. At the same time, physical properties will vary in accordance with the proportions of plasticizer present. This is illustrated in the curves of *Fig.* 17, which apply to elongation, tensile strength, impact strength and compressive strength, of a molding grade of cellulose acetate. Improved molding qualities generally are obtained at some sacrifice of tensile strength, although this may not be objectionable if there is an increase in the toughness. Toughness is determined in various ways, though for the plasticized thermoplastics a rough index of toughness may be ascertained from the tensile product, defined as follows:

TABLE XIII

Properties of Methacrylic Esters

Polymerized Resin	Thermal Yield (degrees Cent.)	Tensile Strength (psi)
Methyl methacrylate	125	9000
Ethyl methacrylate	65	5000
Normal propyl methacrylate	38	4000
Normal butyl methacrylate	30	1500

$$\text{Tensile Product} = \text{Elongation at Break} \times \text{Ultimate Tensile Strength (psi)}$$

In this manner, the effects of elongation, which are even more significant than tensile strength, are taken into account in arriving at the toughness. Still another approach to the evaluation of toughness is a measurement of the area under a stress-strain curve. This index, once again includes elongation and tensile strength, both of which determine toughness.

Temperature: Engineers have acquired the habit of accepting the properties of metals, giving little thought to variation in

physical properties over small temperature variations such as those encountered in temperate zones. For metals, this is satisfactory, inasmuch as only exceptionally low or high temperatures seriously affect the physical behavior. This habit should not necessarily pass on to plastics, which are profoundly affected by changes in temperature. While tensile strength may increase at low tem-

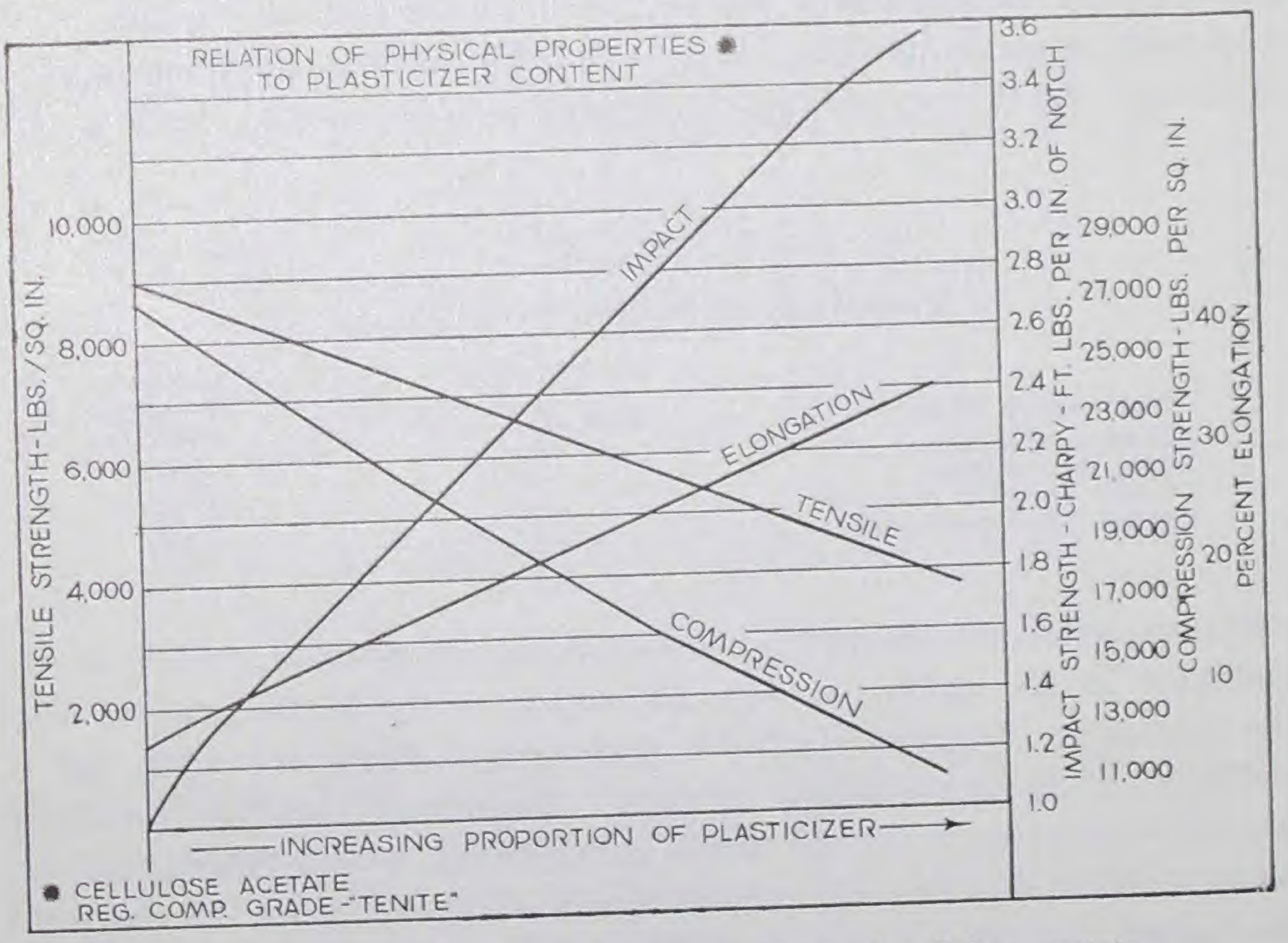

Fig. 17—Effect of plasticizer on properties of cellulose acetate

perature, elongation may fall off much more rapidly, leaving a brittle plastic product. Low-temperature flexibility is a desirable trait if toughness is to be retained. The stress-strain curves reproduced in the accompanying figures show variations encountered in polymethyl methacrylate (*Fig.* 18) taken from a paper by Bartoe* and variations with temperature encountered in cellulose acetate sheet (*Fig.* 19) from a paper by Lawton, Carswell, and Nason**. The large increase in ultimate tensile strength and corresponding decrease in elongation at lower temperatures are apparent for both thermoplastics. In another series of tests, Cars-

*W. Bartoe—*Mechanical Engineering*—Vol. 61, Dec., 1939.
**T. S. Lawton, T. S. Carswell and H. K. Nason—*Mod. Plastics*—22, 145, Oct., 1944.

well and Nason determined the change in ultimate tensile strength of a number of thermoplastics and thermosetting compounds with variations in temperature†. These data demonstrate the greater stability in physical properties of thermosetting compounds (*Fig.* 20). Among the more common thermoplastics, the polyamides (Nylon) offer the greatest tensile strength at the higher temperatures of operation.

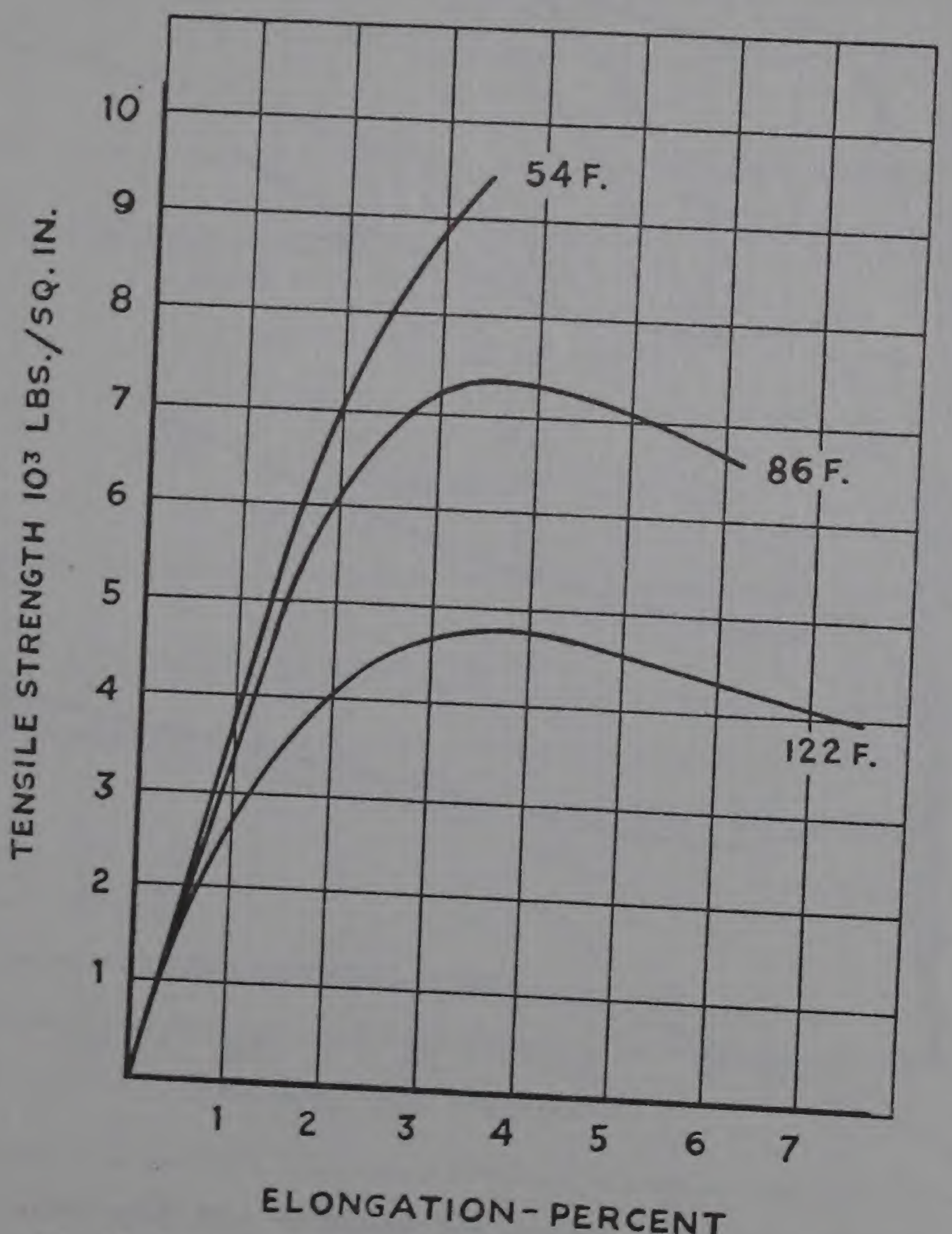

Fig. 18—Dependence of tensile strength and elongation of acrylics on temperature

While these data indicate the effect of temperature upon tensile strength at higher temperatures, there is still another factor to be considered, namely the effect of continuous heating upon the

†T. S. Carswell and H. Nason—*Mod. Plastics*—21, 121, June, 1944.

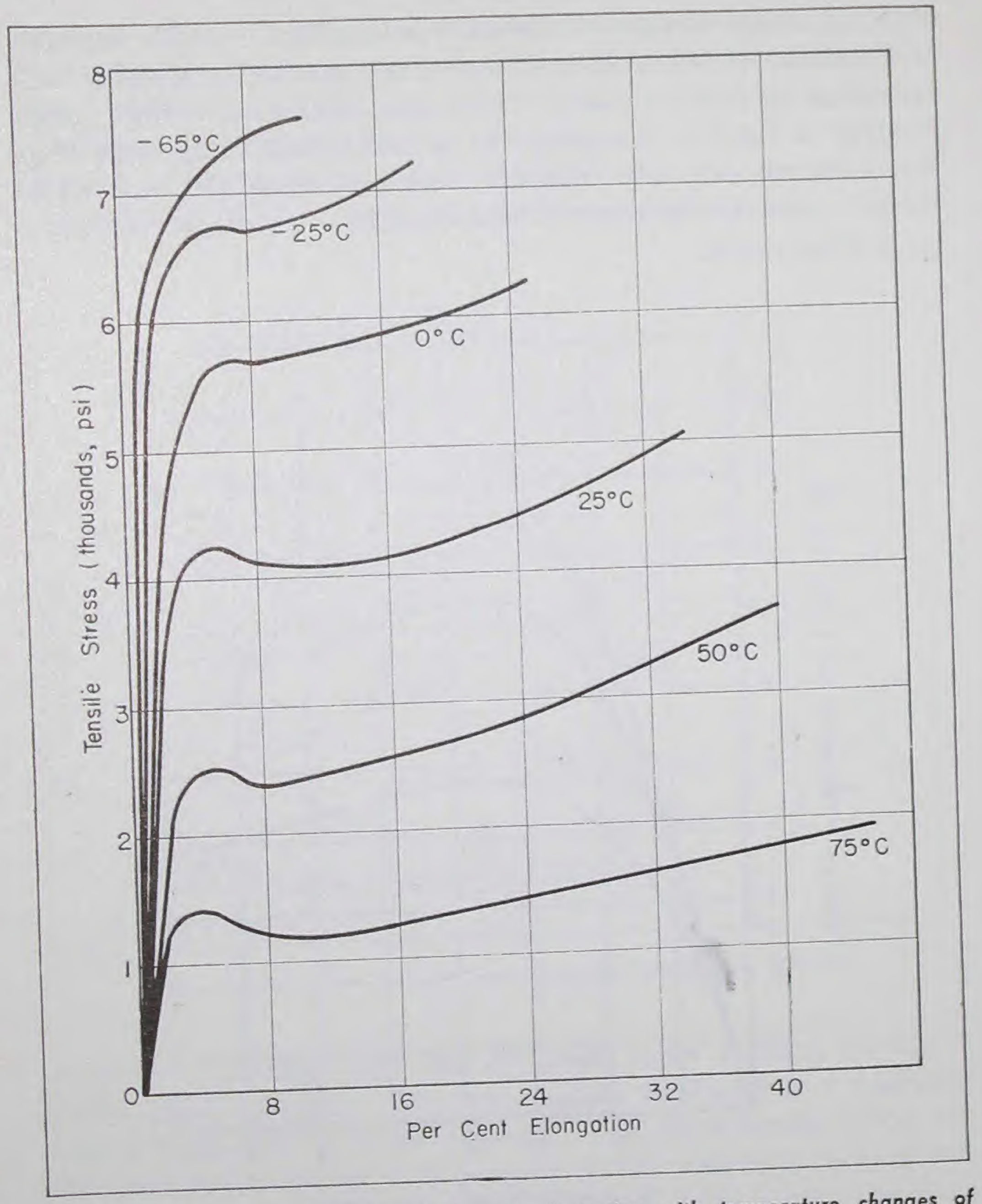

Fig. 19—Variations in tensile strength and elongation with temperature changes of 1/8-inch thick cellulose acetate sheet

tensile strength, measured at room temperature. Not much published data have appeared on this characteristic, though some results will be given for the effects on flexural strength and impact strength. In general, while continued heating at high temperature may entail at first slightly higher tensile strength, due

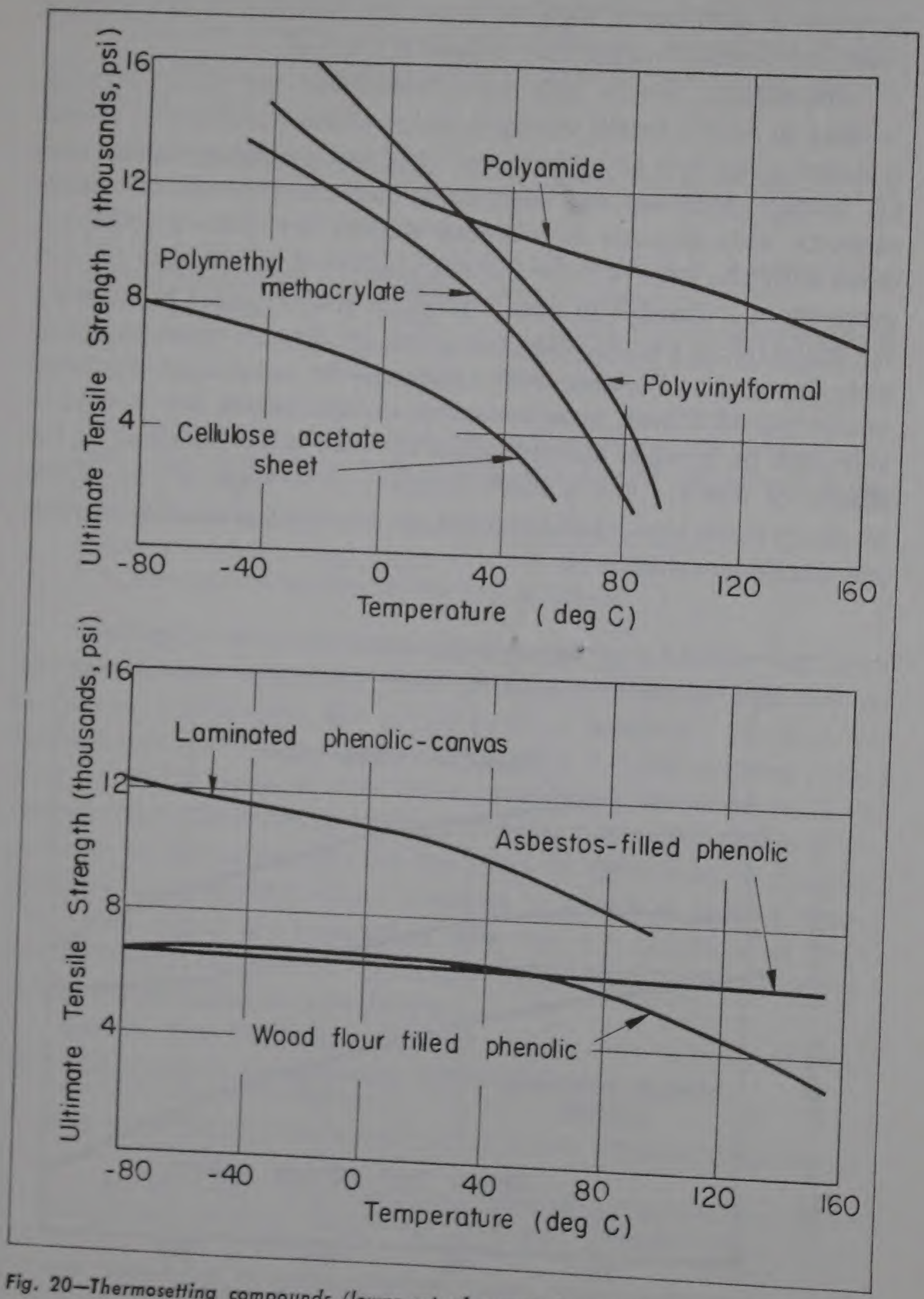

Fig. 20—Thermosetting compounds (lower set of curves) have greater stability of physical properties than do the thermoplastics

to continued polymerization or to loss of plasticizer, if the temperature is sufficiently high to cause deterioration of the filler or resin, the tensile strength may ultimately fall off.

Humidity: Water acts as a plasticizer for many plastics, tending to reduce tensile strength and modulus of elasticity, though increasing ductility and toughness. For water-soluble plastics such as methyl cellulose and polyvinyl alcohol, changes in tensile strength with changes in moisture content are quite pronounced, while with the more water-resistant plastics these changes are less pronounced. Changes in tensile strength with changes in humidity are indicated in *Fig.* 21, data for which are from a paper by Nason and Carswell. Plastics with hydrophillic amino or hydroxyl groups are of course, quite sensitive, though others, low in oxygen and high in halogen content, generally are more resistant to the effects of water. For a more complete evaluation of the effects of water upon plastics the chapter on chemical properties of plastics should be referred to.

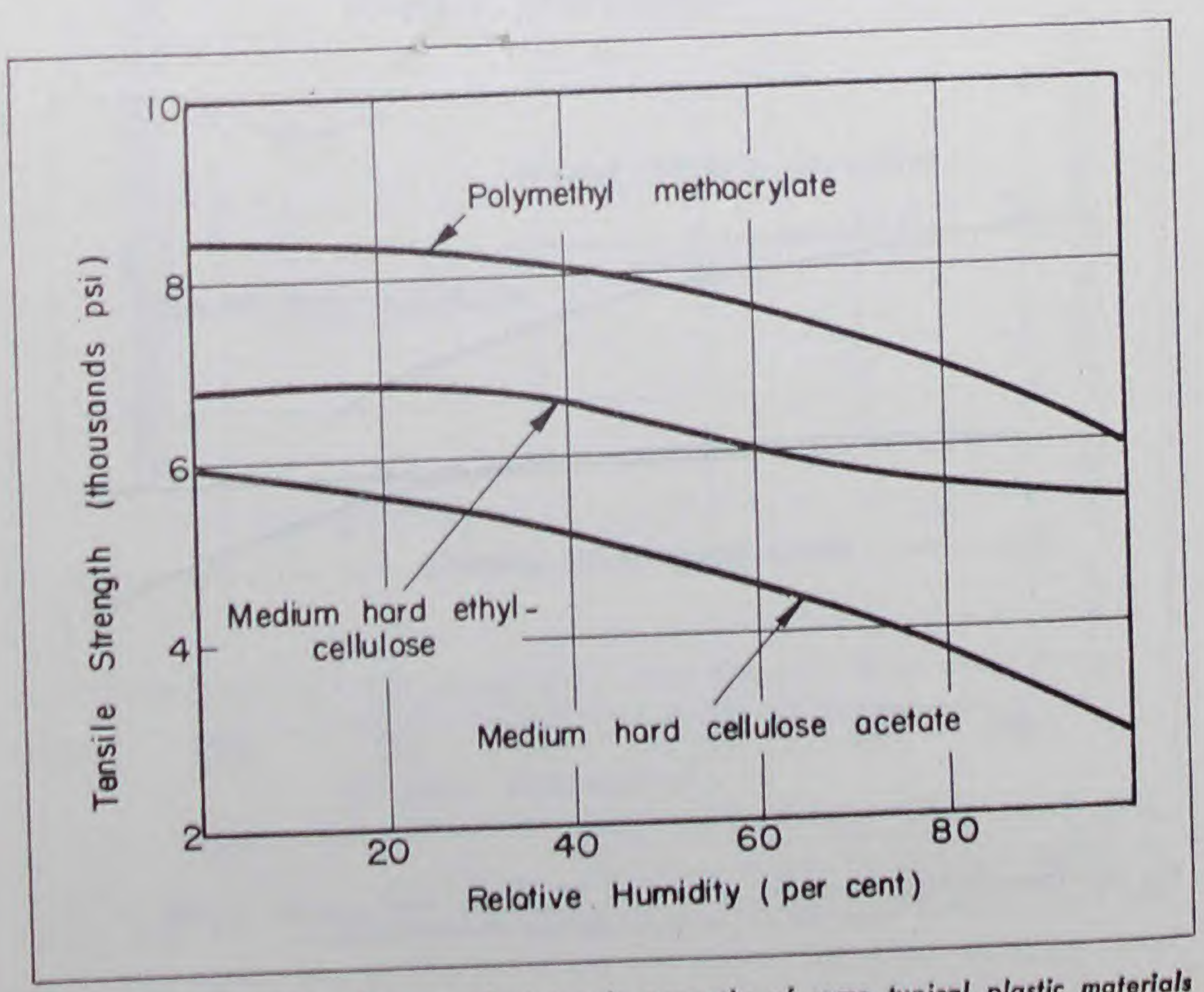

Fig. 21—How humidity changes affect tensile strengths of some typical plastic materials

Methods of Manufacture: The method of manufacturing or fabricating the plastic material may influence the tensile properties appreciably. This may occur in any one of several circumstances, as follows:

(a) During calendering of sheet stock, higher tensile strengths may be observed parallel to the direction of calendering due to the orientation given the outermost molecules
(b) In the extrusion of synthetic or protein fibers, cold stretching will greatly increase the tensile strength of the filament
(c) In the processes of molding, tensile properties of those sections experiencing unidirectional and substantially laminar flow, are higher than those in which a turbulent or non-oriented condition exists. In *Fig.* 22, test coupon A gives a lower tensile strength than test coupon B in which there is substantially unidirectional flow. The thinner the wall section, the greater the difference between A and B.
(d) In the development of laminated products, a preferred grain direction of the laminae, whether it be glass, wood, or cotton, will give anistropic properties to the final laminate.

Bearing in mind the above manufacturing variables, one cannot intelligently apply the data contained in TABLE XIV unless he is acquainted with the manufacturing methods. It must be remembered that the molding conditions for the test samples evaluated by ASTM methods may differ appreciably, for example, from those under which actual molding may be conducted. Hence, differences in properties may be due more to differences in molding qualities than specific values revealed in standard testing methods. The latter are invaluable, however, for qualification tests and screening tests when deciding among a large number of materials for an engineering application.

Tensile Test Methods: Current tensile test methods are described in detail in the following ASTM Specifications:

FOR RIGID ORGANIC PLASTICS—ASTM D-638; "Tensile Properties of Plastics"
ASTM D-651; "Test for Tensile Strength of Molded Insulation"
LONG-TIME TENSILE TESTS—ASTM D-674; "Tensile Tests, Long-Time, of Plastics"
FOR NON-RIGID PLASTICS—ASTM D-412; "Tension Testing of Vulcanized Rubber"

These specifications contain complete details regarding the size and preparation of the test specimens for evaluating the

tensile properties of plastics. For the non-rigid plastics the area under the test jaws of the testing machine is much greater than the reduced area portion because of the great deal of stretch which may take place during test. Rate of speed of testing is dependent upon whether a stress-strain curve is desired, in which case a cross-head speed of 0.05-inch per minute is applied, though for a simple test to destruction 0.2-inch per minute cross-head speed generally is applied for a rigid plastic.

The plastics are particularly sensitive to scratches upon test surfaces, and they should be as free from defects as possible, otherwise the localized stress concentrations may lead to irregular results. This point should be observed particularly when taking elongation data, as no punch or gage marks should be impressed

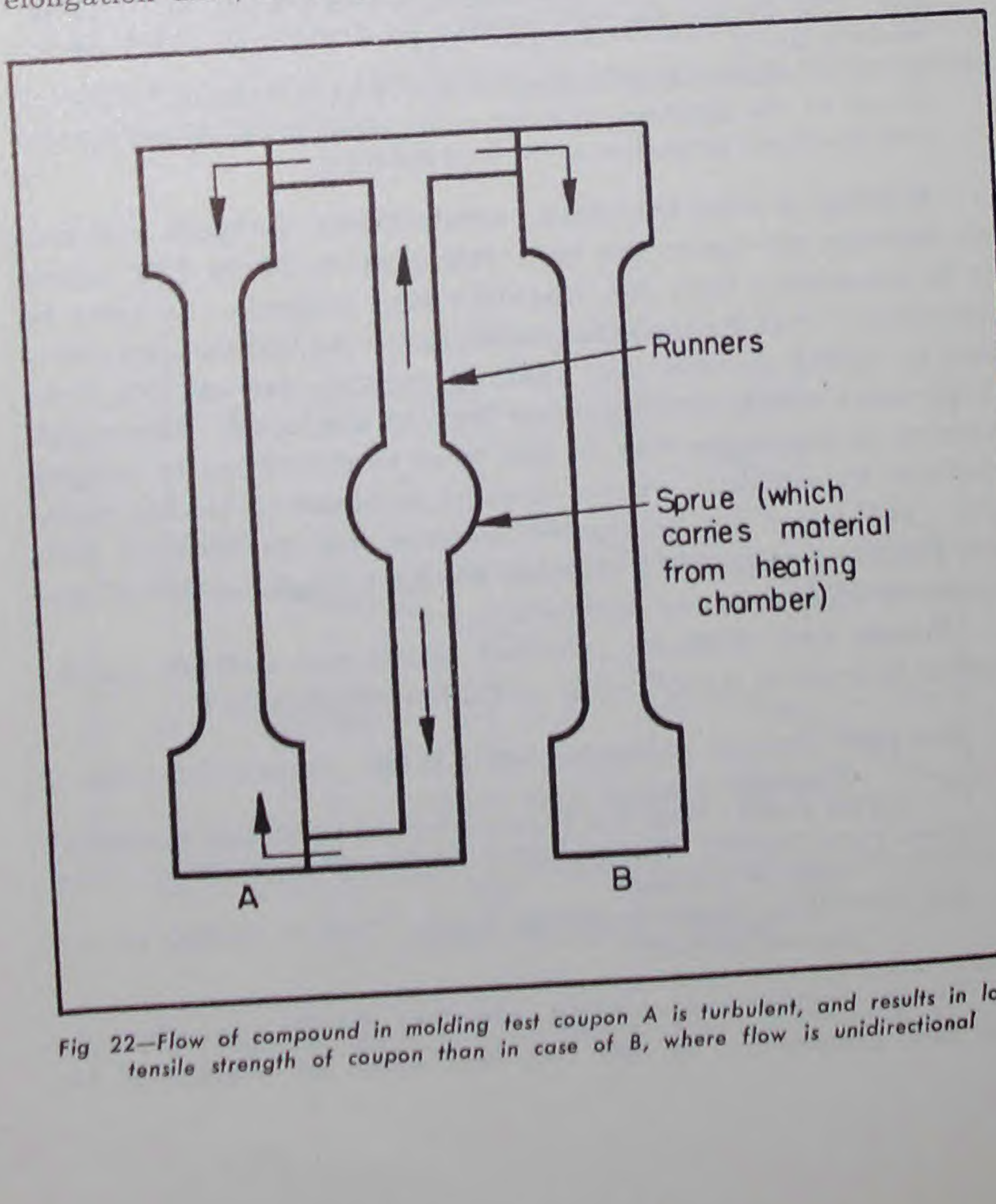

Fig 22—Flow of compound in molding test coupon A is turbulent, and results in lower tensile strength of coupon than in case of B, where flow is unidirectional

TABLE XIV
Comparison of Physical Properties of Plastic Materials§

Plastics	Description	Tensile Strength (psi)	Specific Tensile Strength (psi)	Flexural Strength (psi)	Compressive Strength (psi)
Phenol formaldehyde	Cast resin	5000-10,000	6600	4000-10,000	8000-20,000
molded	Wood-flour filler	6000-11,000	6000	8000-16,000	16,000-35,000
molded	Fabric filler	6000-9000	5500	10,000-15,000	21,000-32,000
molded	Mineral filler	5000-9000	3700	8000-18,000	18,000-36,000
laminated	Pulp preforms	17,000	12,600	25,000	22,000
laminated	Paper base—X *	12,500	8700	21,000	20,000
laminated	Paper base—XX *	8000	5500	16,000	18,000
laminated	Paper base—XXX *	7000	4900	15,000	15,000
laminated	Paper base—special	30,000	22,000	25,000	15,000 (edge)
laminated	Canvas base—C *	10,000	7000	20,000	38,000
laminated	Special canvas weaves	14,000	9700	22,000	44,000
laminated	Fine weave fabric—L *	10,000	7000	20,000	35,000
laminated	Asbestos base	9000	5600	17,000	30,000
laminated	Birch (''Compreg'')	30,000 †	25,000	22,800	23,000
Urea formaldehyde	Birch (''Compreg'')	6000 ‡	5000	13,000	12,000
Melamine formaldehyde	Alpha cellulose filled	8000-13,000	7100	13,500-15,000	25,000-35,000
Polystyrene	Mineral filled	5500-7000	3500	7500-16,500	27,000-37,000
Polymethyl-methacrylate	Molded	5000-7500	5900	6500-10,500	10,000-13,500
Polyvinyl-chloride-acetate	Sheet	6000-8000	5900	12,000-16,000	11,000-15,000
Polyvinylidene chloride	Molded, unfilled	8000-10,000	6700	10,000-13,000	10,000-12,000
Cellulose acetate	Molded	4000-7000	3200	15,000-17,000	....
Cellulose acetate	Sheet form	6000-11,000	6500	5000-16,000	4000-16,000
Cellulose acetate butyrate	Molded	3000-10,000	4500	5000-10,000	12,000-17,000
Polyethylene	Molded	2500-7500	4230	2800-13,000	7500-17,000
Polyamide	Sheet	1700	1850	1700	....
Ethyl cellulose	Molded	9000	7900	13,600	15,000
Cellulose nitrate	Molded	7000-8500	6500	9000-10,000	10,000-12,000
Allyl type	Sheet	5000-10,000	5000	5000-10,000	7000-8000
Polyester	Cast	5000-6000	4170	8000-10,000	21,000-23,000
Aluminum	Laminated glass fabric	30,000-60,000	25,000	40,000-60,000	40,000-50,000
Steel		35,000	13,000	....	....
		60,000	7700	....	....

* Average standards of N.E.M.A.

† With grain.

‡ Against grain.

§ Properties dependent on temperature of test and particular grade of material examined.

on the surface of the plastic. As already noted, some plastics are quite sensitive to atmospheric conditions, and proper conditioning before and after test is imperative in most instances. ASTM D-618; "Conditioning Plastics and Electrical Insulating Materials for Testing" outlines the correct conditioning procedure. The plastics are classified into two types:

TYPE S MATERIALS (*Slow change in properties with varying humidities*)—Conditioned in an air-circulating oven at 122 F to a dry state

TYPE R MATERIALS (*Rapid change in properties with varying humidities*)—Conditioned at a temperature of 77 F and a relative humidity of 50 per cent.

During tensile testing the appearance of the failure often is indicative of the manufacture of the materials. The hard, more brittle types do not have much reduced area portion, and at fracture tend to break into three or more fragments, always with a small additional segment in the immediate vicinity of the failure. On the other hand, the softer, more plasticized varieties

TABLE XV

Long-Time Tensile Strength of Phenolics

Material	Short-Time Tensile Strength at 77 F, 50% R.H. (psi)	Long-Time Tensile Strength, or Estimated Limiting Stress at 77 F, 50% R.H. (psi)	at 192 F (psi)
Phenolic, molded			
Cord filled	6000	2400–2800	900–1200
Rag filled	6100	2400–2800	1200–1400
Woodflour filled ..	6100	2600–2800	1300–1400
Asbestos filled ...	5700	2800-3200	1300-1400
Mica filled	5400	2200-2400	1200-1500

may draw down with pronounced "necking". Laminated materials with a pronounced grain will have tensile failure distributed over a large jagged area, while cross-grain failures are sharp and straight across the test specimen.

Complete tabulations of tensile strengths, flexural strengths, and compressive strengths are given in TABLE XIV. The specific tensile strength is determined by dividing the average tensile strength by the average specific gravity. By this value, plastics compare more favorably with metals, taking advantage of their lower specific gravity. This advantage multiplies in the design of structures where stiffness is a function of the square of the thickness.

Long-Time Tensile Tests: Ultimate tensile strengths deter-

mined by the preceding test methods are far in excess of the safe working stresses, which are more dependent upon the values of the elastic limit. Some highly useful data, TABLE XV, have been obtained for various molded phenolics by Gailus and Telfair*, who report on the limiting long-time tensile strengths of several materials (over 1000-hour period).

Compressive Properties

Many of the limitations and influences upon the tensile properties of plastics also affect the compressive properties. Higher temperatures and high humidities generally bring about some loss in compressive strength. There are certain applications where plastic materials are called upon to exercise good compressive strength; as, for example, in nonmetallic bearings or stretch-press dies for forming sheet metal. The laminates appear to have the highest values of compressive strength, averaging around 40,000 psi, as will be seen in the data listed in TABLE XIV.

When the stress-strain curves of plastics are compared in tension as well as in compression, appreciable differences may be apparent. From an engineering standpoint, especially in stress analysis, this factor makes exact computations of plastic structural elements most difficult, because the majority of formulas are prepared on the basis of equivalence in compressive and tensile values. To illustrate a few typical comparisons, ultimate strength, tangential proportional limit, and modulus of elasticity are compared in TABLE XVI, data for which were obtained at 77 F.

TABLE XVI

Comparison of Tensile and Compressive Properties

	Tensile Properties (typical)			Compressive Properties (typical)		
Material	Ultimate Strength (psi)	Tangential Proportional Limit (psi)	Modulus of Elasticity (psi)	Ultimate Strength (psi)	Tangential Proportional Limit (psi)	Modulus of Elasticity (psi)
Laminated phenolic, canvas base	15,000	2300	1,300,000	27,800	2500	1,600,000
Laminated phenolic, paper base	16,700	4100	1,560,000	23,780	1800	2,150,000
Polymethyl methacrylate	8,000	3300	380,000	12,100	3000	370,000
Polystyrene, molded ...	4,700	2100	469,000	15,200	2200	560,000

* W. Gailus and D. Telfair—Mod. Plastics—22, 449, May, 1945.

When long tubular, or hollow members of plastic materials are to support compressive loads the tendency to buckle should be carefully examined because of the low modulus of elasticity. Compressive members of plastic materials sometimes may be reinforced with other structural elements to support heavy load concentrations.

Compressive Test Methods: Two ASTM test methods cover the technique of testing organic plastic materials in compression. The first requires a special tool for adaptation to a universal testing machine:

1. ASTM D-695; "Compressive Strength of Plastics"
2. ASTM D-649; "Compressive Strength of Electrical Insulating Members"

The latter method was originally developed for laminated phenolic sheet members used as electrical insulating members. Once again, conditioning of specimens before tests is important. Some plastics have such a low modulus and are so ductile that they will continue to flatten out as load is applied, assuming a greater and greater load as the volume of material is spread out over a larger area. Edge compressive tests are particularly significant for laminated sheets, and should be evaluated if structural applications are intended.

A special technique has been developed for evaluating the deformation of plastics under compressive loading at elevated temperatures (ASTM D-621-43; "Deformation of Plastics Under Load at Elevated Temperatures"). Test specimens which are small cubes measuring ½-inch by ½-inch are placed under a dead weight of 1000 pounds, while deformation is read over a 24-hour period. Most plastics possess a decided elastic "memory", and while they may deform quite appreciably under a heavy load, will tend to recover their original shape if left unstressed or if heated slightly.

Shear Strength

Data on the shear strength of the various plastics are of fundamental importance to the design of structural elements. In TABLE XVII are listed typical values of shear for various plastics, obtained with the aid of a punch and a die. These data will also permit computations on the load required to shear or punch

a given section from a sheet stock of plastic, once the shear area is calculated.

Shear strength, like other physical properties, will depend on temperature and humidity, specimen sizes, and manufacturing conditions. For example, molded phenolics with a shear strength of 10,000 psi at room temperature will drop to 8,000 psi at 200 F, and 6000 psi at 325 F. The punch and die technique is quite valuable in establishing rapid tests upon manufacturing variables. The author has found* that a small punch and die mounted in an arbor press with a recording scale measuring the load, may be conveniently used to determine the shear strength of molded ther-

TABLE XVII
Shear Strengths of Plastics

Material	Form	Shear Strength (psi)
Phenolic	Cast	7000
Phenolic, general-purpose	Molded	10,000
Phenolic, fabric base	Laminated	14,000
Phenolic, paper base	Laminated	12,500
Urea, standard medium	Molded	8000
Polymethyl methacrylate	Sheet	8200
Cellulose acetate	Sheet	6000
Ethylcellulose	Injection molded	7500
Polyethylene	Sheet	950
Polystyrene	Injection molded	8000
Polyvinyl chloride-acetate	Injection molded	10,500
Allyl type	Cast, unfilled	4800

mosetting plastics after different times of cure. In the results shown in *Fig.* 23, typical phenolic and urea plastics approximately 1/16-inch thick were molded at 310 F and tested after different intervals of cure.

It is also possible to obtain data on the load-deformation characteristics in shear. Generally, results will be dependent upon the thickness of the sheet specimen, because the thinner the sheet, the higher the ratio of bearing to shear area, and the greater the apparent shear strength. Data obtained by the author with the aid of an ASTM Johnson shear tool are illustrated in *Fig.* 24. Deformation of a sheet approximately 0.160-inch thick was obtained. Punch diameter was 1.000-inch and the load was applied on a universal testing machine.

Shear Test Methods: The ASTM specification for the evaluation of shear strength with the aid of a shear punch and die is: ASTM-D 732; "Shear Strength of Plastics". Another meth-

*J. Delmonte—*ASTM Bulletin*—114, 25, Jan., 1942.

od widely used involves a cylindrical specimen and a three-plate jig developing double shear: Federal Spec. L-P-406a, Jan., 1944. These methods were compared for a number of plastics and results reported by Schwartz and Dugger*.

Flexural Strength

The flexural strength or the transverse strength of plastics is subject to the same set of variables which influence the other physical properties, including temperature, humidity, and many manufacturing variables. This value is readily determined without costly equipment and numerous molders or laminators find it expedient to run control tests on the properties of their materials with flexural strength as the variable physical factor. The

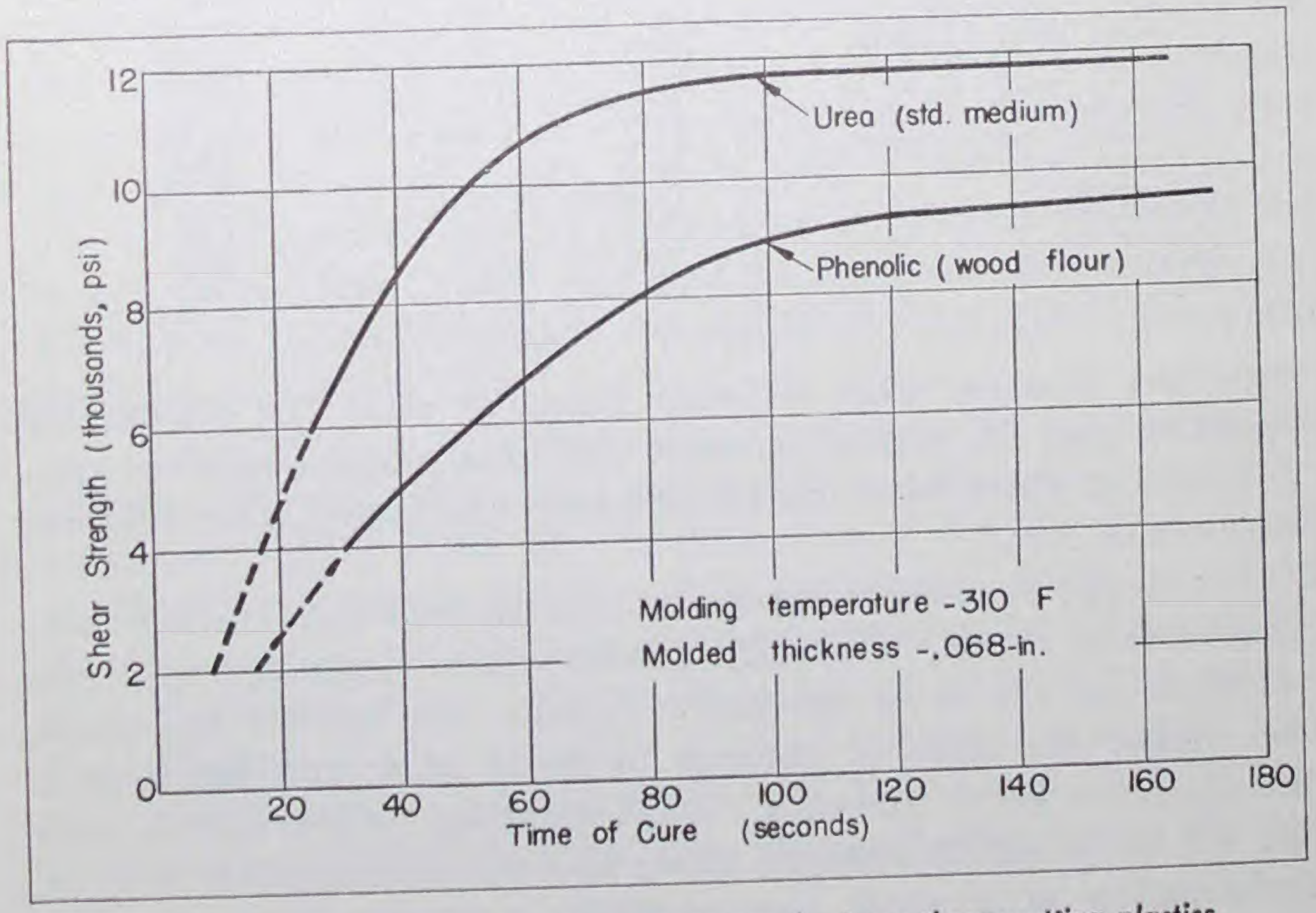

Fig. 23—Shear strengths at various cure intervals of two thermosetting plastics

technique, which is described more fully in the standard specifications noted below, tests flat specimens of sheet or molded plastics, supported at two ends and loaded at the center. Ratio of

*R. Schwartz and E. Duggar—*Mod. Plastics*—21, 117, March, 1944.

span to thickness is preferably at least 16 to 1 (Fed. Spec. LP 406a), though others permit an 8 to 1 ratio. The former ratio is recommended when modulus of elasticity in flexure is to be determined. Zinzow, in summarizing a group of flexibility tests, reported negligible effect of loading edge radius, though dependence of results on rate of loading.*

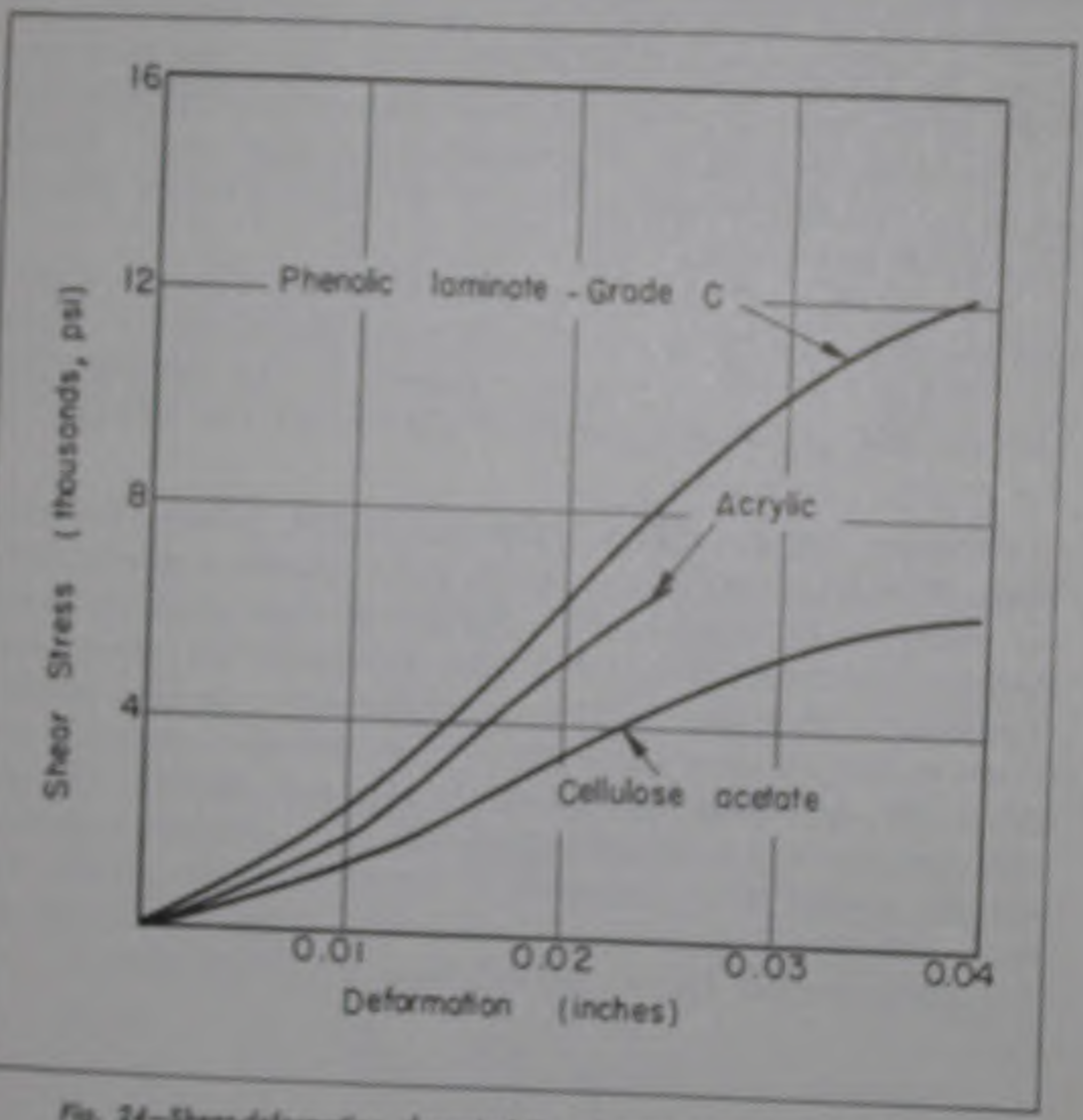

Fig. 24—Shear-deformation characteristics of some typical plastic sheets

The nature of the filler in molded plastics, or the nature of the laminae in laminated plastics decidedly influence the flexural strength value obtained for various plastics. The highest values among the molded materials occur in long-fiber-filled phenolic compounds, or resin-pulp molded preforms. Thermoplastics such as

*W. A. Zinzow—*ASTM Bulletin*—134, 22, May, 1945.

the polyamides or the higher temperature-resistant polystyrenes also possess exceptional values, although materials such as the polyamides (nylon) may change from a flexural strength of 18,000 psi, at 0 per cent moisture to 11,000 psi at 2 per cent moisture, and 8500 psi at 3 per cent moisture. The highest flexural strengths among the laminates have been obtained for the low pressure laminated, glass-cloth reinforced materials, where flexural strengths of 60,000 to 70,000 psi are obtained consistently. Of course, much higher experimental laboratory values have been realized. In all cases, however, the most important contributing factor has been the exceptional strength of the glass cloth. Representative flexural strength values of the more common plastics are given in TABLE XIV.

The influence of temperature on the flexural strength of several plastics is shown in *Fig.* 25 which reproduces data of Nason and Carswell**. The superior properties of the thermosetting phenolic and melamine formaldehyde laminates are indicated in this sketch.

Flexural Strength Test Methods: ASTM D-650; "Flexural Strength of Electrical Insulating Materials", covers a general testing procedure for evaluating the flexural strength of various solid electrical insulating materials. Test specimens are conditioned according to procedure D-618 as described earlier in this chapter in the section on tensile strength. Sheet and plate materials are tested with specimens turned both flatwise and edgewise, and cut both crosswise and lengthwise of the sheet. A reference specification for testing these materials is ASTM D-229-43; "Tests for Sheet and Plate Insulation". When calculating the maximum fiber stress for flat sheets, the following formula is used:

$$S = \frac{3\,Pl}{2\,ba^2}$$

where S is the maximum fiber stress, P the applied load in pounds, l the distance between supports in inches, b the width of specimen in inches, and a the depth of specimen in inches.

Modulus of elasticity sometimes is determined from deflection observed during the bending of test specimens during flexure. This affords a relatively simple method of determining the modu-

**T. S. Carswell and H. K. Nason—*ASTM Symposium*—1944.

lus experimentally. Area under the load-deformation curve obtained in flexure testing has also been a good index of the relative toughness of the material.

Modulus of Elasticity

For engineering design problems requiring a stiff structural member, the majority of plastic materials are unsuited unless designed with reinforcing ribs. Compared to steels with a modulus of elasticity of 30,000,000 pounds per square inch and aluminum in the neighborhood of 10,000,000 pounds per square inch, the range of moduli for plastic materials (200,000 to 2,000,000 pounds per square inch), seems rather inadequate for the job. However, there are miscellaneous engineering designs which require these low moduli of elasticity for the load-deformation characteristics imparted to the structural member. The low modulus signifies

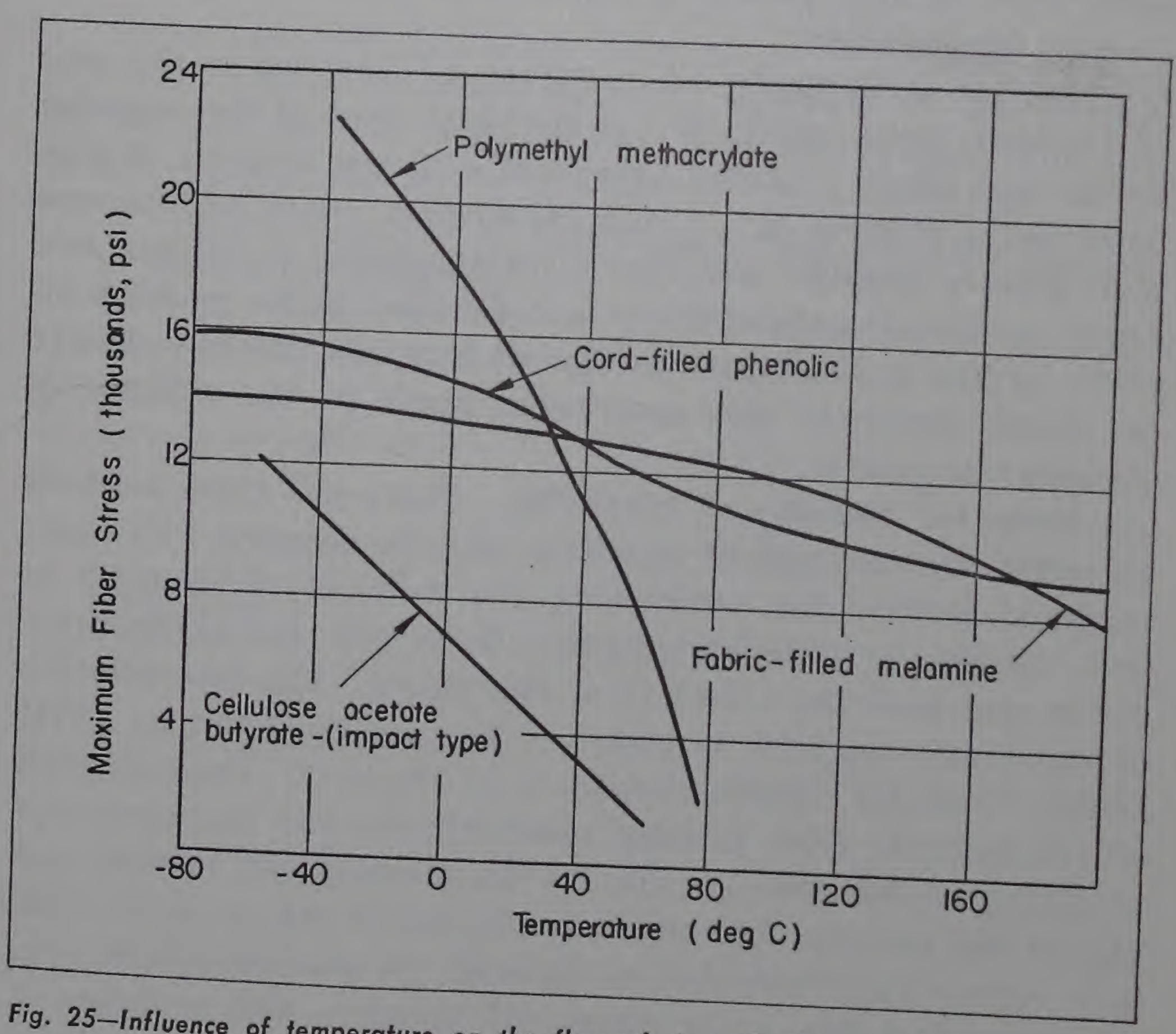

Fig. 25—Influence of temperature on the flexural strength of a variety of representative plastics

high resiliency. This resiliency has been the keynote of quiet operation of plastic gears, connoting the ability to deform enough under impact loading, to absorb shock stresses which otherwise lead to noisy operation. Resiliency may be expressed as an inverse function of the modulus of elasticity.

It must be pointed out again that the modulus of elasticity, as determined from the slope of the initial portion of the stress-strain curve, is also a function of the tension in the fabric weave of laminated plastics, nature of filler, and plasticizer content or molecular weight of thermoplastic substances. Determination of the slope of the stress-strain curves for a plastic material within the proportional limit is not easily done. The straight line portion is not always obvious, appearing sometimes as a well-rounded curve. It has also been suggested that the modulus of elasticity be represented as a time-dependent function, depending on plastic flow. Moduli of elasticity may also be shown to be dependent upon temperature, exhibiting appreciably higher values below freezing temperatures.

Modulus of elasticity, when defined, is described as the ratio of the unit stress within the proportional limit of the material, to the unit strain. Closely associated with the modulus of elasticity is the stiffness in a structural member, which will increase with greater moduli. For structures employing a stressed skin (such as aircraft) the stiffness is a function of the modulus divided by the specific gravity. In other words, the low density of plastic materials also contributes much to the stiffness of stressed skin designs.

Tests for Modulus of Elasticity: There are three methods by which the modulus of elasticity may be obtained. The conventional method for determining the modulus of elasticity in pure tension or pure compression, is to plot the stress-strain curves and read the values from this figure. The determination of the tensile modulus is described in accurate detail in ASTM D-638; "Test for Tensile Properties of Plastics". Determination of the modulus from bending measurements has the advantage of giving an integrated result for compression and tension, and also in the rapidity with which measurements can be made. This is a rather important feature because, as pointed out shortly, creep and cold flow under stress will interfere with accuracy of strain measurements which are time consuming by the conventional

testing technique with strain gages and the standard dumbell test specimen.

Two techniques are available for measuring the modulus in bending: Simple cantilever beam, with support at one end (this method is more sensitive) and simple beam with two supports and load applied at the center (as in flexure).

Simple cantilever beam—load at end $\quad \text{Modulus } (E) = \dfrac{Wl^3}{3 \times I \times d}$

Simple beam supported at two ends—load at center $\quad \text{Modulus } (E) = \dfrac{Wl^3}{48 \times I \times d}$

where d = deflection at point of loading
l = length of beam
W = weight
I = moment of inertia

Creep and Cold Flow

Creep and cold flow phenomena of plastic materials are of particular interest to design engineers, inasmuch as they indicate the physical behavior of plastics under sustained load. The plastic deformation, *Fig.* 26, is comprised of two components:

Creep—Early part of plastic deformation, when the time rate of deformation is changing

Cold Flow—Time rate of deformation is substantially constant, and attained after creep period has passed.

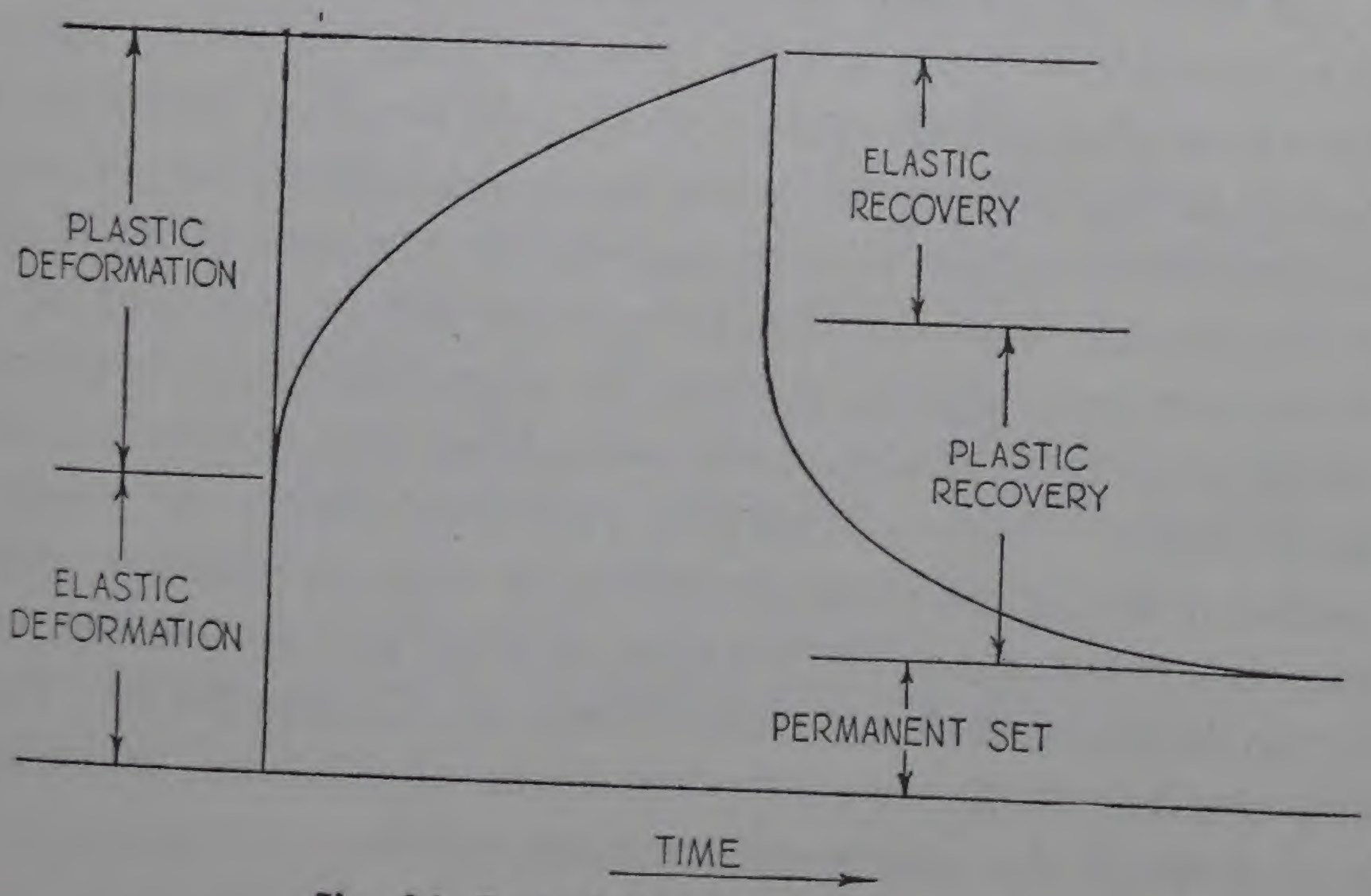

Fig. 26—Typical time-deformation curve

The phenomena of creep and cold flow may also be better understood by referring to *Fig.* 27 which shows the mechanical analogy of the molecular structure of a plastic material. This mechanical model permits instantaneous elastic deformation immediately upon application of load and immediately upon removal of load, no matter how long the load has been applied. The author has observed that these two values of elastic deformation and elastic recovery are exactly equal when the material is stressed within the elastic limit*. Plastic deformation will occur at the smallest stresses, even below the elastic limit, though at a much less severe rate. Plastic recovery will not, however, necessarily equal the plastic deformation, being dependent upon three variables: (1) Temperature, (2) magnitude of stress, and (3) time stress was applied. These phenomena occur for all plastics, though more so for thermoplastics than thermosetting types. This means that screws and nuts or rivets which clamp sheets of plastics material together may be expected to loosen in time. This is due to creep and cold flow which relieve the applied stresses after the members have been tightened.

For the best overall picture of the effects of creep and cold flow, a three-dimensional chart showing stress, log-time, and deformation is most satisfactory. In *Fig.* 28 charts for laminated phenolic, canvas base, and polymethyl methacrylate sheet are shown. These results may be compared with the curves in *Fig.* 29 which demonstrate actual deflection measurements of a simple cantilever beam employed in making creep measurements.

The prevailing temperature has quite an influence upon the rate of creep and the effects of creep. In another series of tests to determine the effects of creep upon permanent set, a number of plastics were loaded at a maximum fiber stress of 1000 psi as simple cantilever beams. The permanent set in per cent of original deformation is shown in *Fig.* 30 after four days loading and four days recovery. These data more than any others emphasize the temperature limits of certain plastics because of creep.

Data on the creep characteristics of various plastics, obtained at room temperature, a fiber stress of 1000 psi, and in the simple cantilever beam technique, are shown in TABLE XVIII. The resistance coefficient, R, was obtained from calculations based on the constant slope of the plastic deformation curve.

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*J. Delmonte—*ASME Trans.*—Vol. 62, 513, Aug., 1940.

Elastic Limit and Proportional Limit

Exact determination of the elastic limit of a plastic material is not an easy matter, particularly when creep phenomena are admitted at very low stresses. Elastic phenomena occur instantaneously and, with that thought in mind, it was suggested in the first edition of this book ("Plastics in Engineering"—First Edition—1939, Page 171) that by close examination of elastic deformation and elastic recovery, it was possible to determine the elastic limit, when the ratio of the elastic deformation to elastic recovery began to increase with higher and higher stress values.

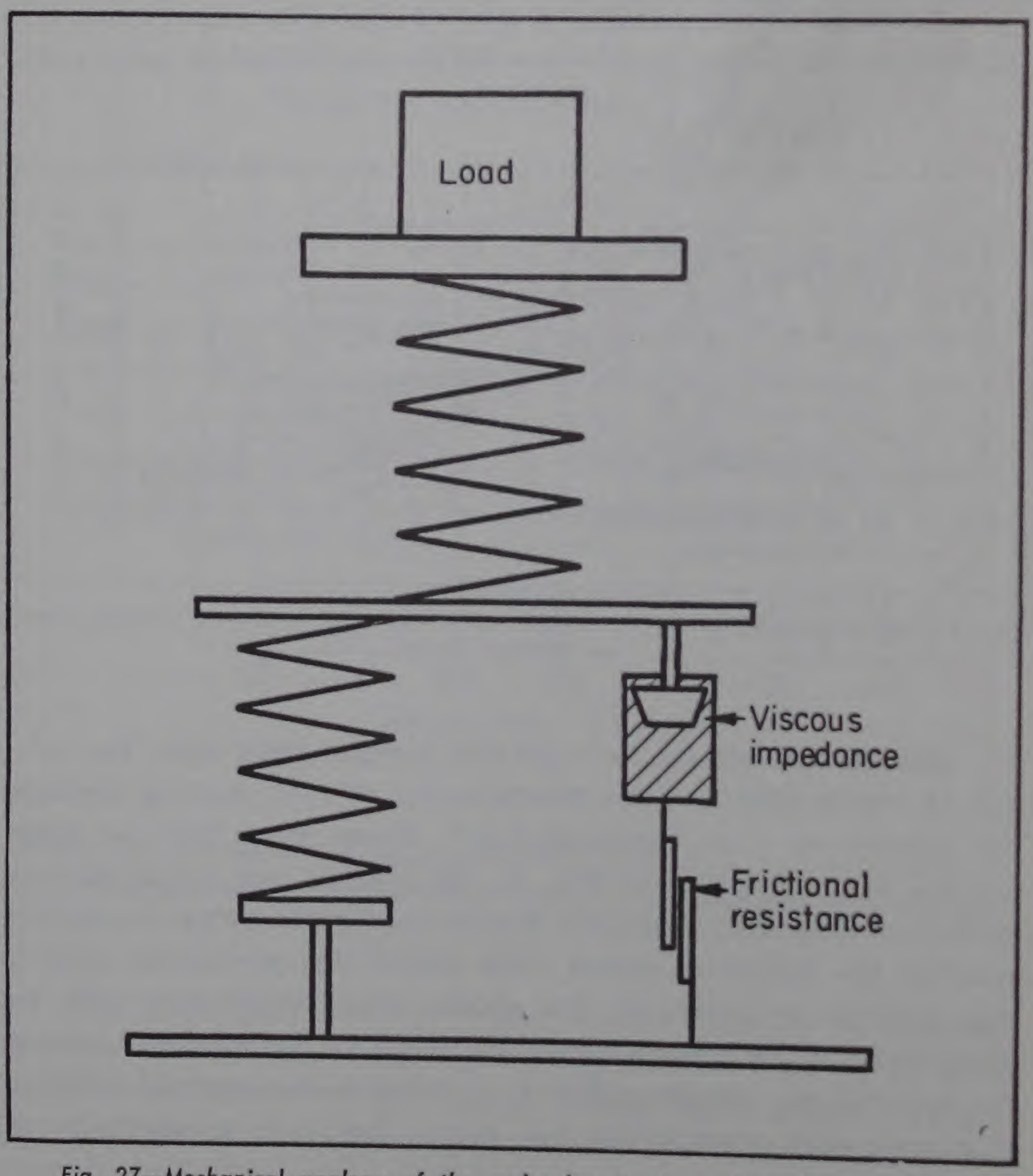

Fig. 27—Mechanical analogy of the molecular structure of a plastic material

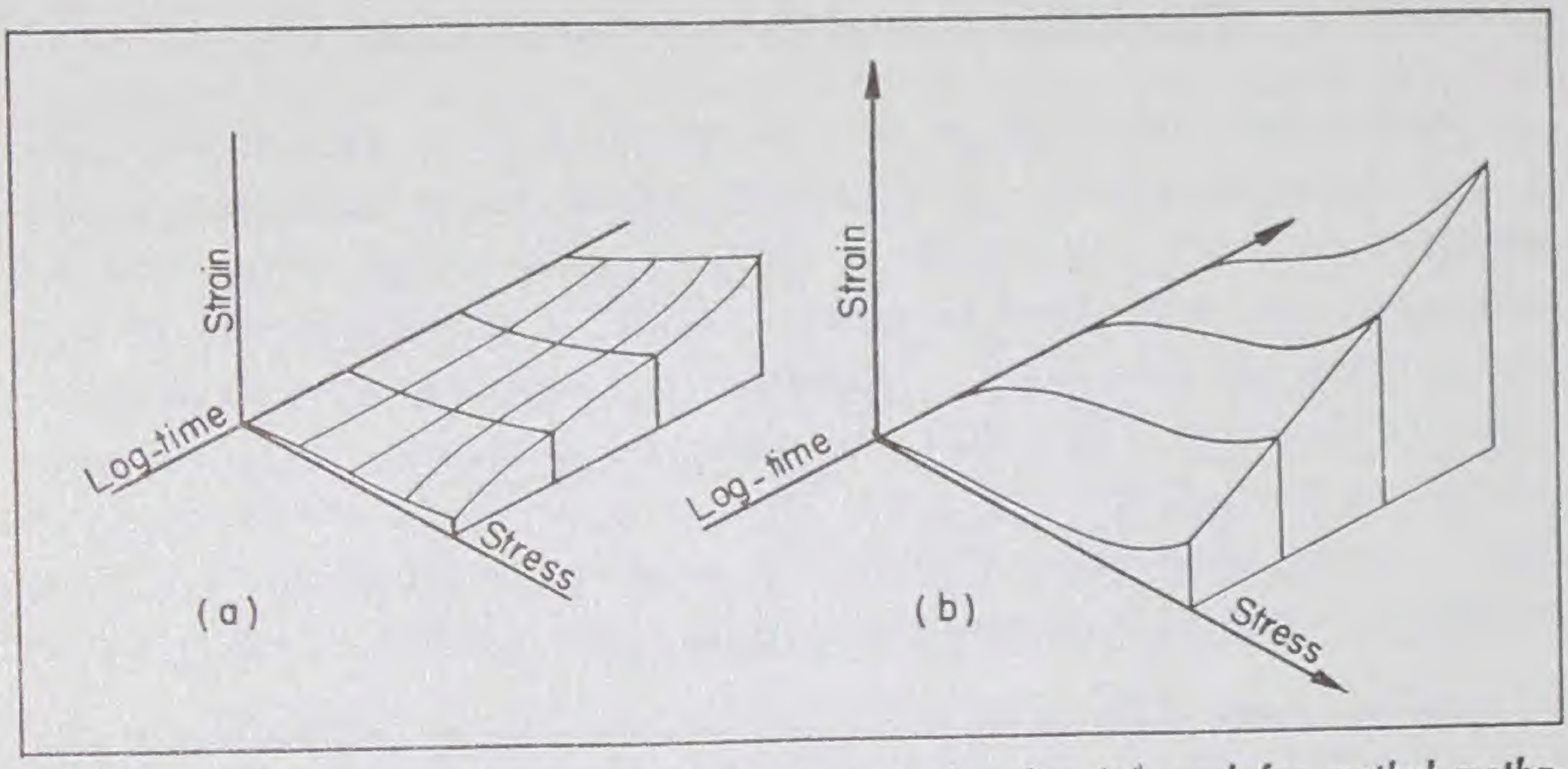

Fig. 28—Strain-stress-log time curve for laminated phenolics (a), and for methyl methacrylate (b)

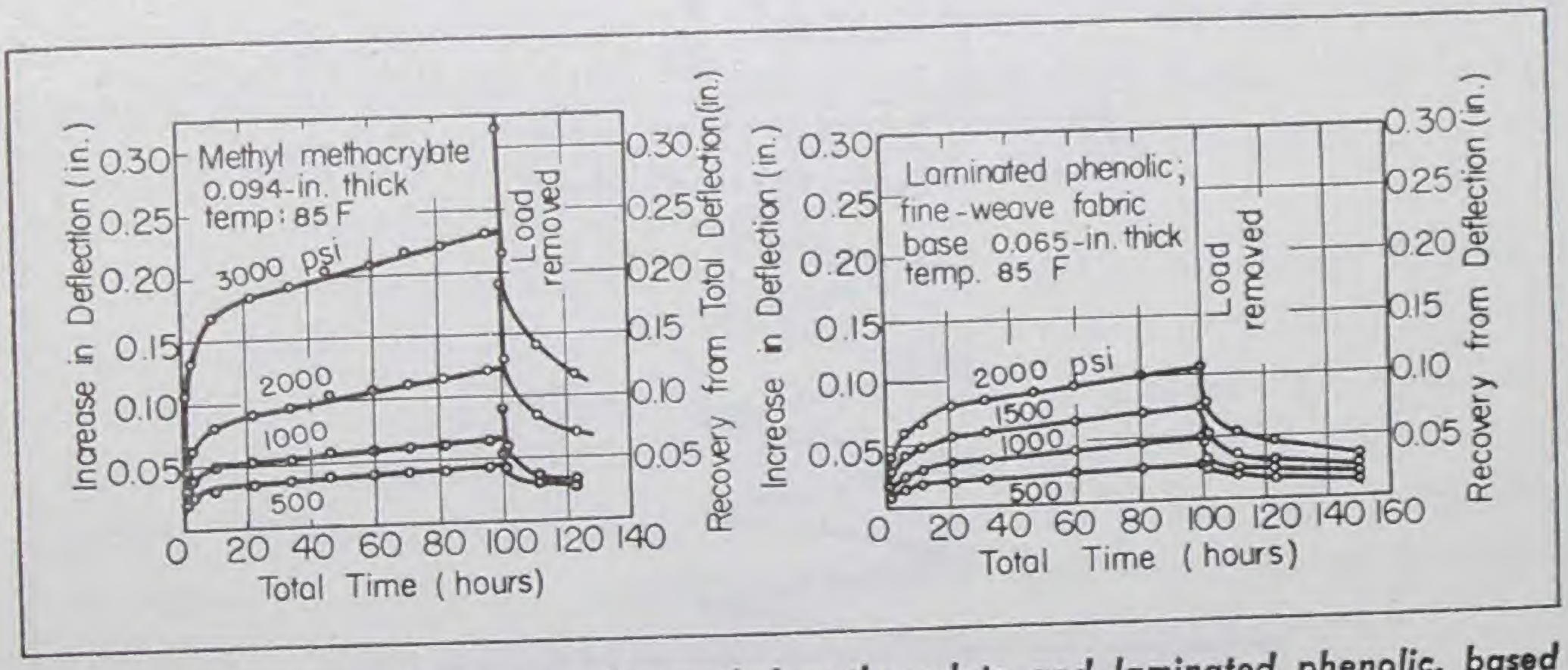

Fig. 29—Time-deformation curves for methyl methacrylate and laminated phenolic, based on 100-hour tests

More recent efforts have thrown further light upon the subject of elastic limit and the determination of safe working stresses for plastics at room temperatures.* These tests laid the basis for the data appearing in *Fig.* 31. By loading and unloading test specimens as simple cantilever beams and by observing the spread between the deflection curves (this constitutes permanent set), it was possible to arrive at the elastic limit, which may also be interpreted in the case of plastic materials as the maximum stress the material can assume without incurring permanent set. Creep, of course, may occur below this value, though it is substantially

*J. Delmonte—*Machine Design*—16, 99, Dec., 1944.

recovered upon removal of load. Maximum safe working stresses may be read directly from *Fig.* 31, where curves intercept the axis.

Determination of the proportional limit is not an easy matter for some plastics because the curves of stress-strain do not break sharply, and the point of tangency is ill-defined. These data do

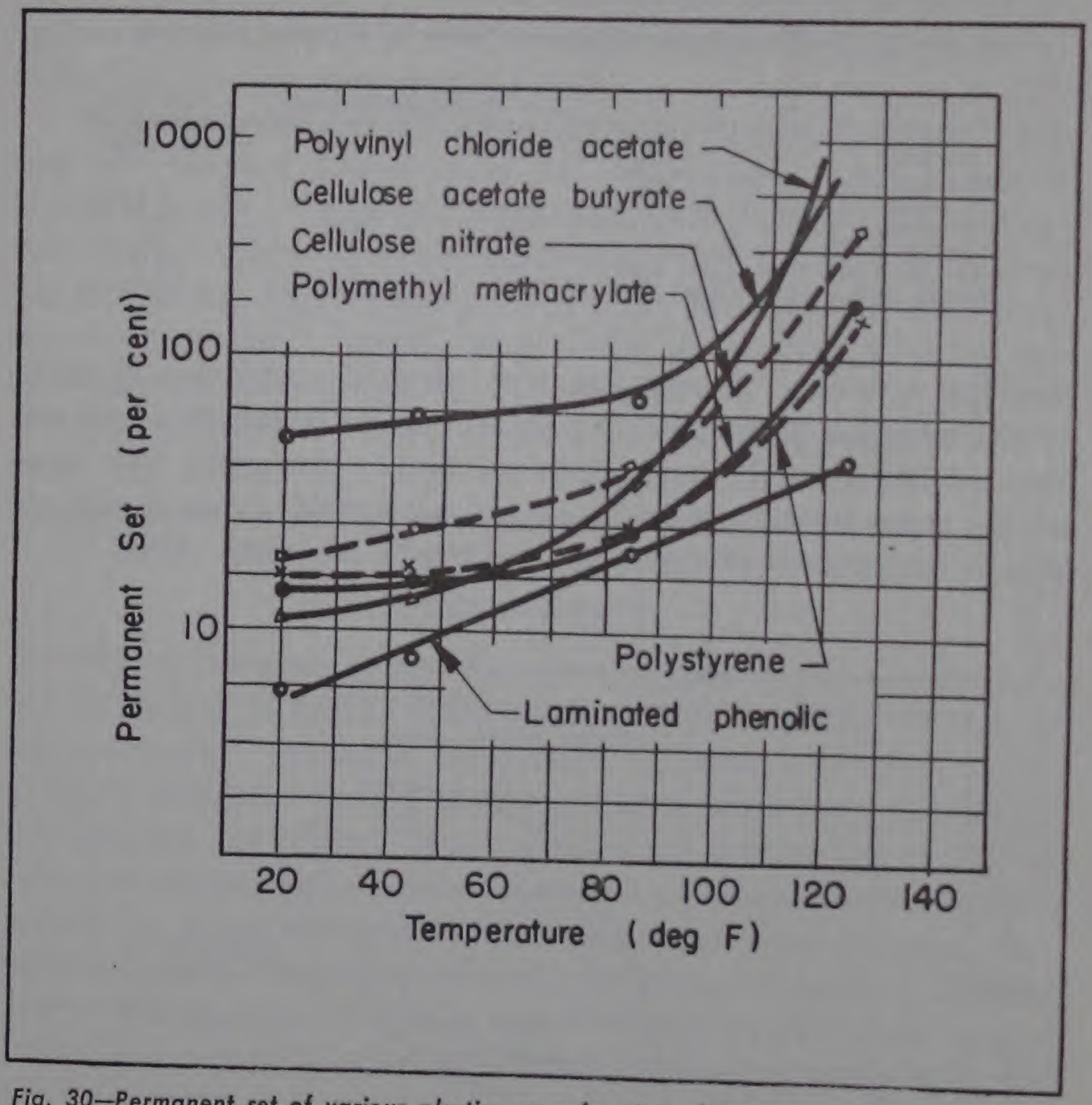

Fig. 30—Permanent set of various plastics as a function of temperature after 100 hours as simple cantilever beam (max. fiber stress, 1000 psi.)

not have much practical significance in the selection of working stresses for plastics, as they generally are too high to be safe for most materials. Even higher, though more positive values are obtained by the off-set proportional limits, determined, for example, at 0.05 per cent or 0.2 per cent off-set along the defor-

mation curve. These values are too high, however, for safe working stresses.

The yield strength of some plastics, such as ethylcellulose, may readily be determined by a sharp reverse curve in the stress-strain data though once again the values are too high for safe

TABLE XVIII

Creep and Cold Flow Characteristics of Various Plastics

Material	Plastic Deformation (% of elastic deformation) at 1 hour (%)	Plastic Deformation (% of elastic deformation) at 100 hours (%)	Cold Flow Coefficient ($R \times 10^6$)
Polyvinyl chloride-acetate filled sheet	4.9	26.0	1.66
Polystyrene, molded	3.2	24.0	2.50
Cellulose acetate sheet	16.1	66.0	0.50
Laminated phenolic, fabric base	7.2	22.0	9.08
Methyl methacrylate sheet	6.7	14.6	4.54

working stresses. Among the high strength laminates of glass or Mitscherlich pulp, yield strengths may be about 50 to 60 per cent of the ultimate compressive or tensile strength. For some of the more brittle materials, compressive yield strength and ultimate compressive strength are practically the same value.

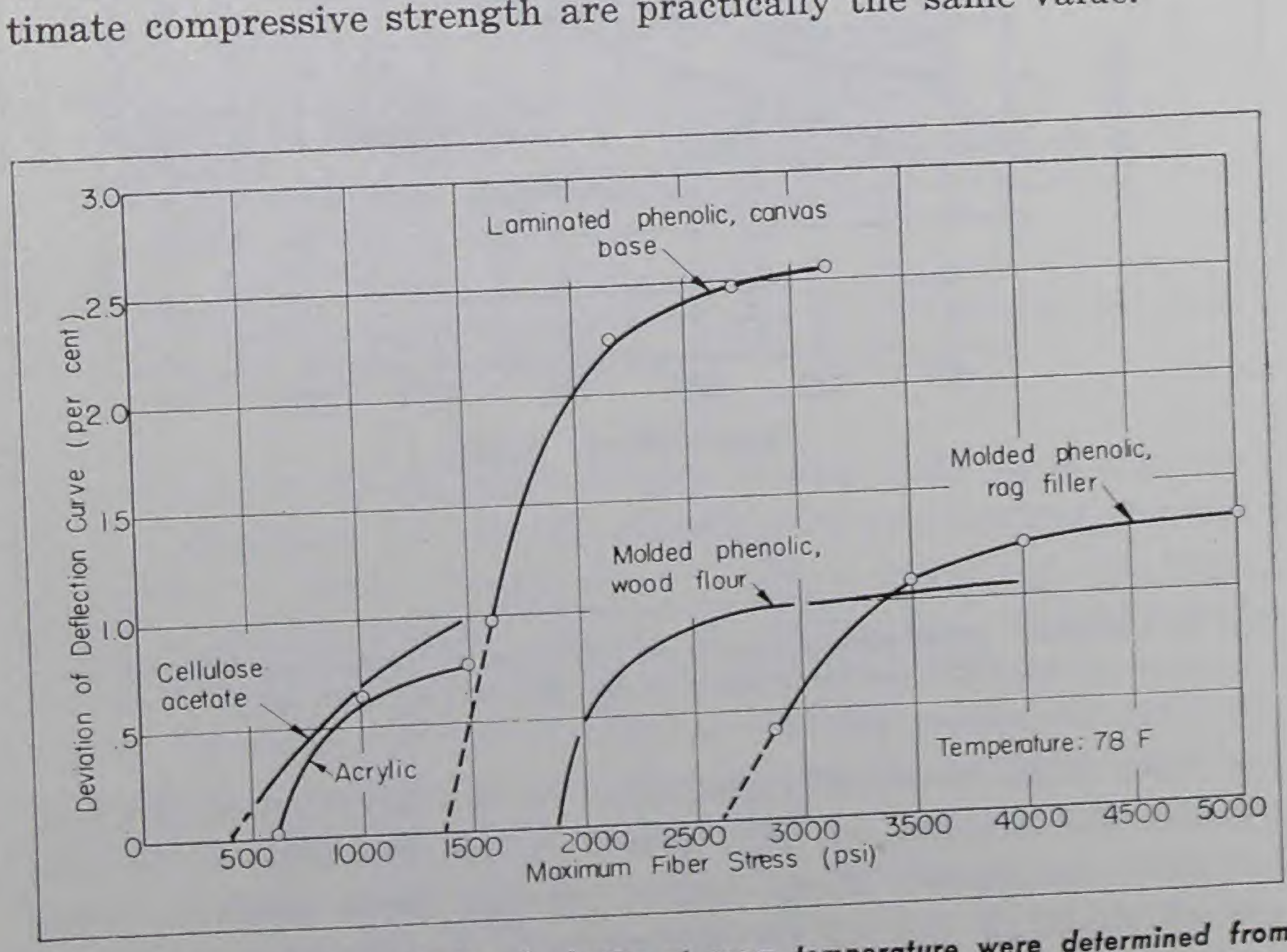

Fig. 31—Apparent elastic limits of plastics at room temperature were determined from interpretation of these curves

Fatigue Limit

Fatigue data upon plastic materials are not too abundant, though recent tests have given some assistance in this direction. Oberg, Schwartz, and Schinn performed a number of interesting fatigue tests upon plastics at different temperatures and in a notched and un-notched condition. Using the rotating-beam fatigue testing machine, some of the results they obtained are illustrated in *Fig.* 32. At lower temperatures, the curves moved higher on the corresponding charts.*

Test Methods: A number of fatigue testing methods have been proposed for plastic materials. Many of these are described in ASTM D-671; "Flexural Stress, Repeated (Fatigue) of Plastics, Test For". While this specification describes a fatigue testing machine of the fixed cantilever type, others, including the application of torsional, direct compression or tension stresses are mentioned in the appendix to this specification. In testing fatigue strength of plastics, variables such as frequency, size of specimen, rate of heat loss from the specimen, and other factors affecting specimen temperature will influence the observed results.

Impact Strength

One of the most widely discussed physical properties of plastics is impact strength. This property has been the subject of much attention primarily because of occasional failures in improperly designed molded plastics, which create the impression that plastics are brittle. Some plastics are brittle, though others have exceedingly high impact strengths. In no one single property is there so much variation between one plastic and the next. Impact properties also reflect the efficacy of the molding technique. In the manufacture of molded and laminated goods for the armed forces, the development of high-impact-strength plastics was concentrated upon and noteworthy results achieved. In earlier discussions on fillers for molding compositions, the prime importance of the filler as a factor in controlling impact strength was pointed out, though the less desirable surface finish of the high impact strength fillers was noted. Nevertheless, a dark uniform lustrous surface may not always be imperative in distinctly engineering

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*T. P. Oberg, K. T. Schwartz and D. A. Shinn—*Modern Plastics*—20, Page 87, April, 1943.

applications, and the utilization of shredded fabric fillers brings about desirable results in molded products from an impact standpoint.

In some applications, the impact strength obtainable from phenolic-molded, shredded-fabric-filled plastics has been inadequate

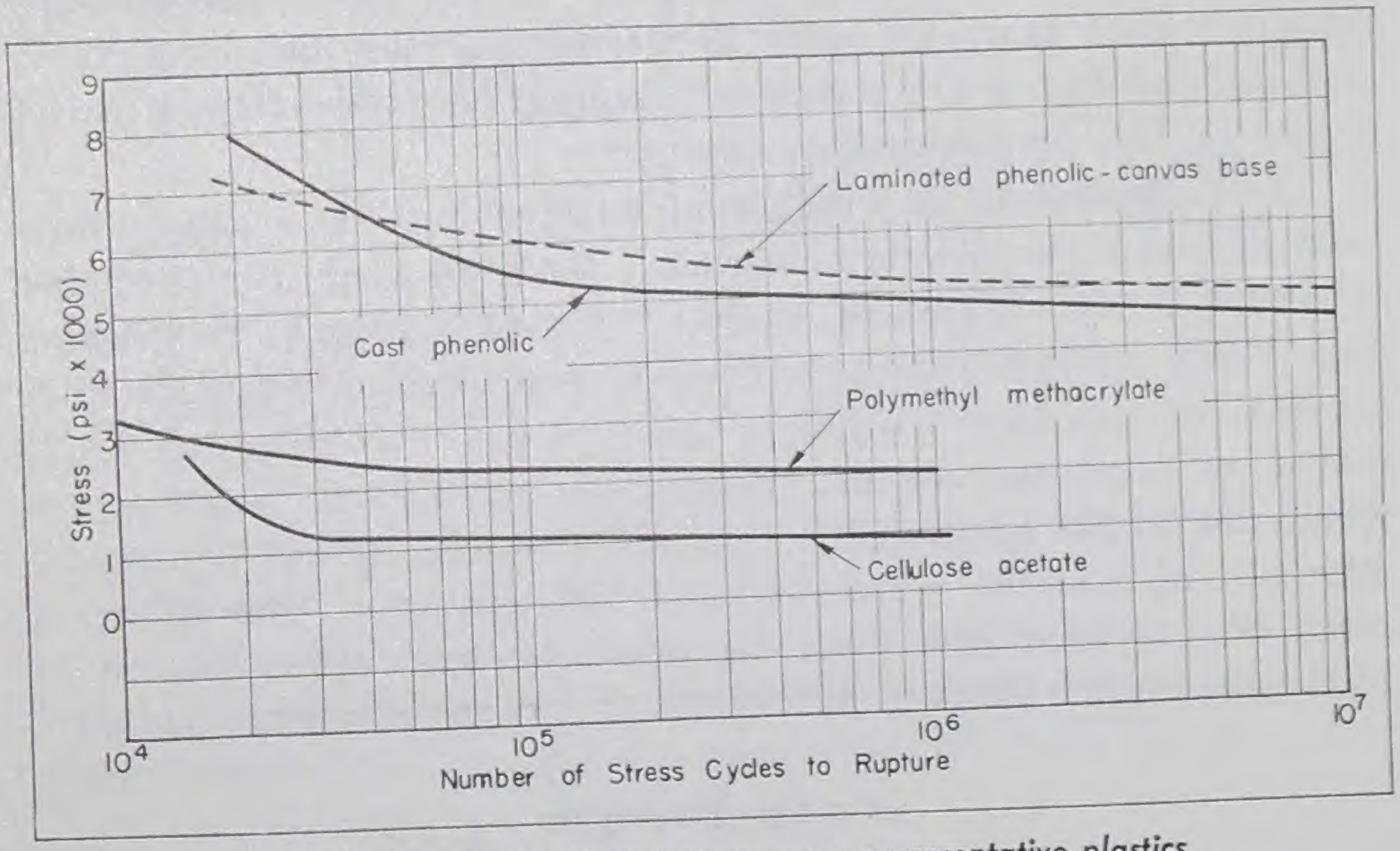

Fig. 32—Results of fatigue tests on some representative plastics

for the circumstances involved. Reinforcement of weak sections by laminated materials, molding board, or a metal core have helped conditions considerably.

The comparative impact strength of various phenolic plastics is brought out in TABLE XIX, though more exact values are given in TABLE XX, listing several physical properties of plastic materials.

One of the most important of the influences upon the impact strength of plastics is temperature, and some of the results of Nason and Carswell (loc.cited) are reproduced in *Fig.* 33. The majority of the thermoplastics and some of the thermosetting compounds increase their impact strength appreciably when raising from cold to higher temperatures. In fact, in applications of the hot-melt cellulose derivatives as tools for forming sheet metal, it is the practice to warm them slightly before operating to give the tools added impact strength.

TABLE XIX
Comparison of Impact Resisting Qualities for Phenolic Materials

Material	Filler	Relative Impact Strength
Molded	Mica	2
Molded	Asbestos	2.5
Molded	Woodflour	1-3
Molded	Cotton	4
Molded	Shredded fabric	6
Molded	Long fabric fiber	12
Laminated	Kraft paper	10
Laminated	Fabric base	20
Laminated	Wood veneer base	35

While the standard Izod and Charpy impact tests will be described shortly it is well to note that these tests are performed upon bars produced under a set of molding conditions which may be considerably different from the molding of an engineering article. Consequently it is recognized that standard impact tests are most useful in the selection of compounds for a given job, though in the last analysis a service test is the final proof. Laboratories such as the Fire Underwriter's Laboratories, have devised tests upon the final molded articles, such as plugs and receptacles, by the simple expedient of dropping them against a hard pine board a specified number of times. This procedure will also explore molding as well as material variables. Interest has been growing not in single-blow impact failures, but in repeated impact tests, involving certain fractions of the single-blow re-

TABLE XX
Comparison of Physical Properties

Plastic	Description	Izod Impact Strength (ft lb/in. notch)	Flexural Modulus of Elasticity (psi $\times 10^5$)	Rockwell Hardness
Phenol formaldehyde	Cast resin	0.30-0.40	3.0- 6.0	M 80-M 85
Phenolic, molded	Woodflour	0.24-0.40	8.0-11.0	M115-M120
Phenolic, molded	Fabric filler	3.00-4.00	8.0-11.0	M115-M120
Phenolic, molded	Mineral, asbestos	0.24-0.32	15.0-25.0	M 95-M115
Phenolic, laminated	Paper, Grade X	1-7	10.0-15.0	M 90-M120
Phenolic, laminated	Canvas, Grade C	2-15	10.0-15.0	M 90-M120
Urea formaldehyde	Molded, cellulose	0.24-0.36	15.0	M118-M122
Melamine formaldehyde	Mineral filler	0.28-0.40	16.0	M112
Polymethyl methacrylate	Sheet	0.20-0.60	3.0- 5.0	M 60-M 80
Polystyrene	Molded	0.26-0.60	4.0- 4.7	M 55-M 95
Polyvinyl chloride-acetate	Rigid	0.25-0.50	3.5- 3.8	....
Polyvinylidene chloride	Molded	0.30-1.00	0.5- 1.0	M 50-M 65
Cellulose acetate	Molded (Flow-286 F)	1.30-3.80	1.3- 1.9	R 86-R112
Cellulose acetate-butyrate	Molded (Flow-286 F)	1.80-5.30	1.2- 1.7	M 25-M 49
Cellulose acetate	Sheet, general	1.00-3.00	2.0- 3.5	R105-R115
Polyethylene	Sheet	3.0 plus	0.15	R 27
Polyamide	Molded	0.6-0.94	3.0- 3.2	M 80-M 90
Ethyl cellulose	Molded	3.0-11.0	1.0- 5.0	R 20-R110
Cellulose nitrate	Sheet	3.0- 6.0	1.5- 3.0	R 90-R120
Allyl resin (CR-39)	Cast	0.3- 0.4	3.0	M 95-M100
Aluminum—24ST	Rolled	20.0	100.0	....

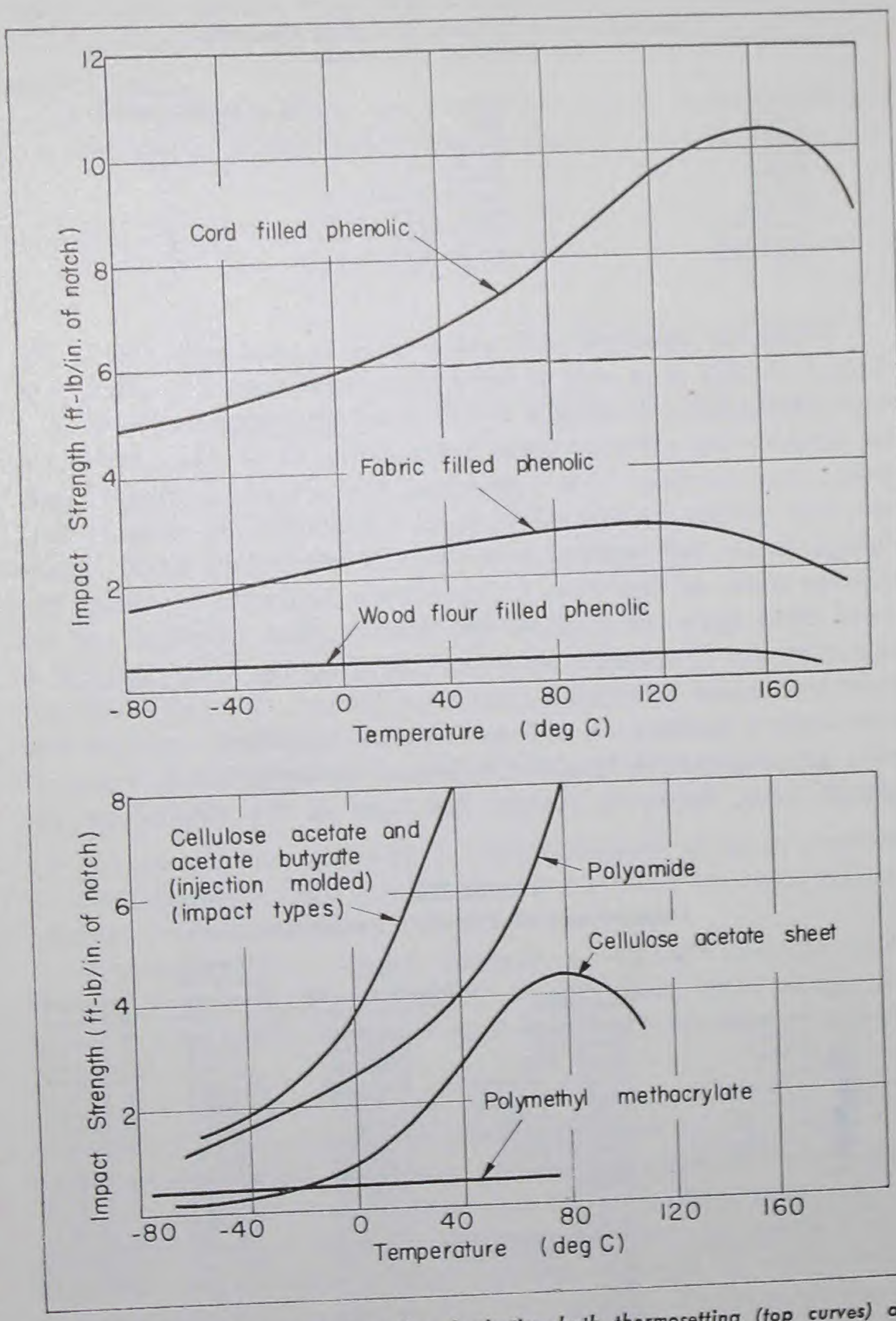

Fig. 33—In general, impact strengths of plastics—both thermosetting (top curves) and thermoplastic (bottom curves)—improve with rising temperature

sults. These tests are determined by a method worked out at Bell Telephone Laboratories, involving a ball falling on a sharply inclined plane.* Repeated impact limits determine those values which can be applied indefinitely without fracturing the plastic for the test conditions employed. Typical results are given in the TABLE XXI.

While molded and laminated phenolic plastics possess the most satisfactory physical properties over a wide range of temperatures, prolonged exposures to high temperatures may lead to deterioration of the properties, particularly impact strength. Attention is invited to the chapter on thermal properties where some of these data are given.

TABLE XXI

Material	Relation of Repeated Impact Blow to Single Impact Blow
Polymethyl methacrylate	50%
Polystyrene	40%
Molded phenolic	27%
Cellulose acetate-butyrate	5%
Nylon	58%
Phenolic laminate, canvas base	45%
Phenolic laminate, paper base	50%

Impact Test Methods: Impact tests upon plastic materials are valuable in ascertaining the relative toughness of the specimens and are indicated by the energy absorbed in breaking a standard test specimen under the blow of a pendulum. Two conventional methods are employed, the Charpy and the Izod test (ASTM test method D-256). However, drop tests upon finished molded articles are also invaluable inasmuch as impact strength is profoundly dependent upon the nature of resin flow.

1. CHARPY TEST—The specimen is held as a simple horizontal beam and it is broken by a blow delivered midway between supports. The specimen size is shown in *Fig.* 34. Tests may be conducted upon a notched or un-notched specimen.

2. IZOD TEST—The specimen is held as a vertical cantilever beam and the specimen broken by a blow delivered a specified distance from a clamped edge. A notched specimen as shown in *Fig.* 35 is required for the test. Laminated sheet materials should be tested edgewise and flatwise. It is customary to condition

*P. M. Field—*Mod. Plastics*—21, 125, April, 1944.

molded pieces in a drying oven at 50 C (122 F) for 48 hours. Tests usually are conducted on several specimens and an average value determined.

Other impact test methods are also being explored, including guillotine techniques, which have won favor in some laboratories. Others have determined the minimum amount of energy

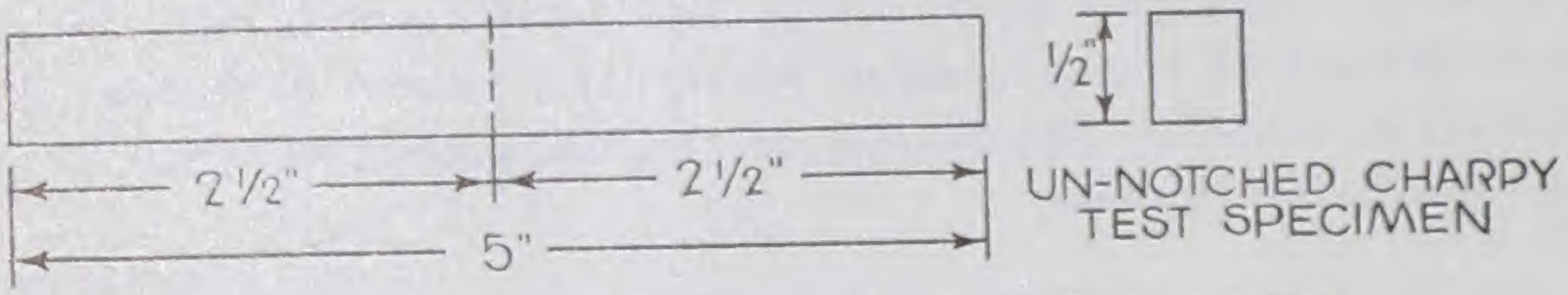

Fig. 34—Charpy impact bar; ASTM standard test specimen

to just fracture the impact test specimens, avoiding the losses incurred when the impact blow travels through. The opinion has been expressed that rupture occurring under impact arises from the same basic considerations as those governing flexural failures.*

Surface Hardness

The hardness of the surface of a plastic material may be interpreted in many ways. If the material is to resist indentation, such as may the surface of some laminate, a hardness test based upon indentation methods is important. On the other hand, if the plastic is to withstand the scratching of a needle for a molded phonograph recording disk, scratch resistance is important. If a transparent plastic bomber nose is to be exposed to the abrasive action of a sand storm, abrasion resistance is most important. There is no one single plastic outstanding in all respects of surface hardness and it is necessary to examine the various methods of evaluating hardness, and select that technique applicable to the immediate problem.

In general, plastics scratch rather readily upon their surface, which may interfere with the clear vision of a transparent sheet or mar the surface of a polished molded part. Some of the newer synthetic resins prepared from the polyester resins are

*L. Welch and H. Quackenbos—*Trans. ASME*—68, 547, July, 1946.

quite an improvement over softer earlier types, though increased surface hardness is usually accompanied by lower impact strength. It appears that the optimum solution lies in a tough, resilient core and a surface film of a hard, abrasion-resistant material. Hardness of phenolic moldings may be improved in part through various mineral fillers, though a thin resin film which develops on the outside during molding is the portion first subject to attack. This resin layer acts as a protective film to some extent and various properties such as electrical characteristics and moisture resistance depend upon its presence. Consequently, when plastics are affected readily by abrading actions, changes may be expected in other surface properties. The soft surface of plastics is self-evident on examination of slightly used transparent sheets of various thermoplastic materials, such as the cellulose deriva-

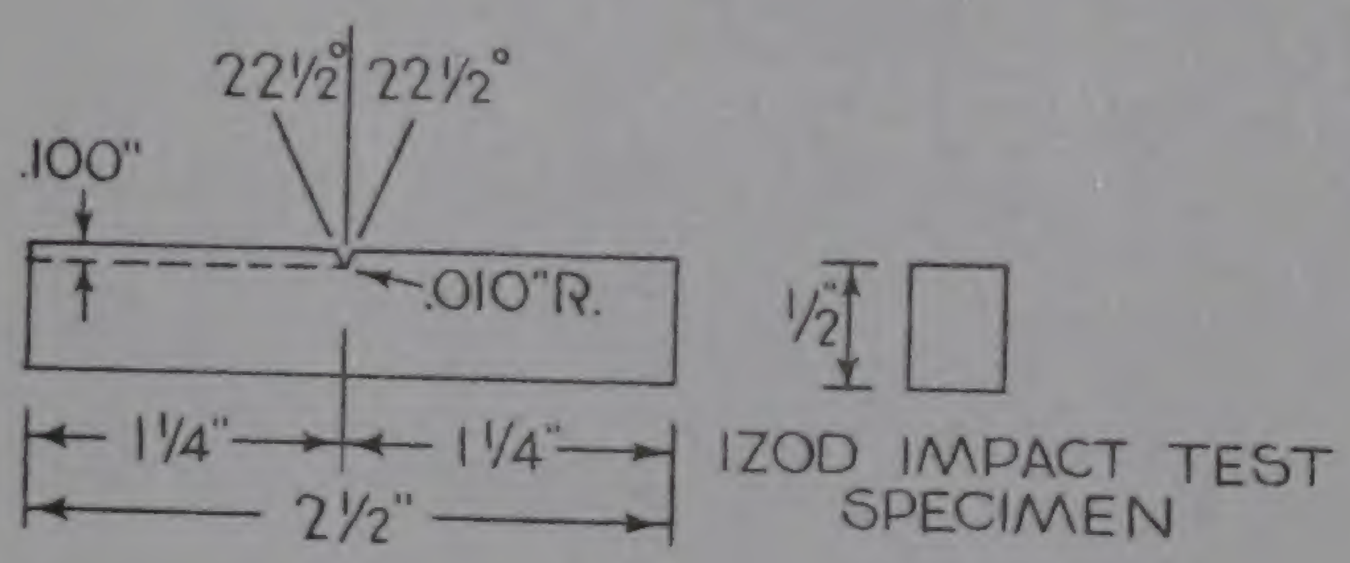

Fig. 35—Izod Impact bar; ASTM standard test specimen

tives, vinyl resins, acrylic resins, etc. When fresh from the manufacturer, these sheets are above criticism from an optical viewpoint. Comparatively short periods of handling or exposure will reveal the presence of a few scratches or scars, which ordinarily would not occur on glass plate.

In spite of their apparent softness in Rockwell or Brinell hardness tests, plastics will wear better than metals in certain gear and bearing applications, where their resiliency can be utilized to advantage. In fact, in gear trains, alternating the plastic with a metal gear results in a mechanism which will outwear all-plastic or all-metal combinations.

Most plastic materials have their own particular pattern when scratched and examined under a microscope. Two typical photomicrographs and their explanatory notes appear in *Fig.* 36.

Not only is the width of the scratch significant, but also its depth and the appearance of the edges along the scratch. The more brittle materials form a rough, uneven edge, as though the material cleaved off as irregular crystals.

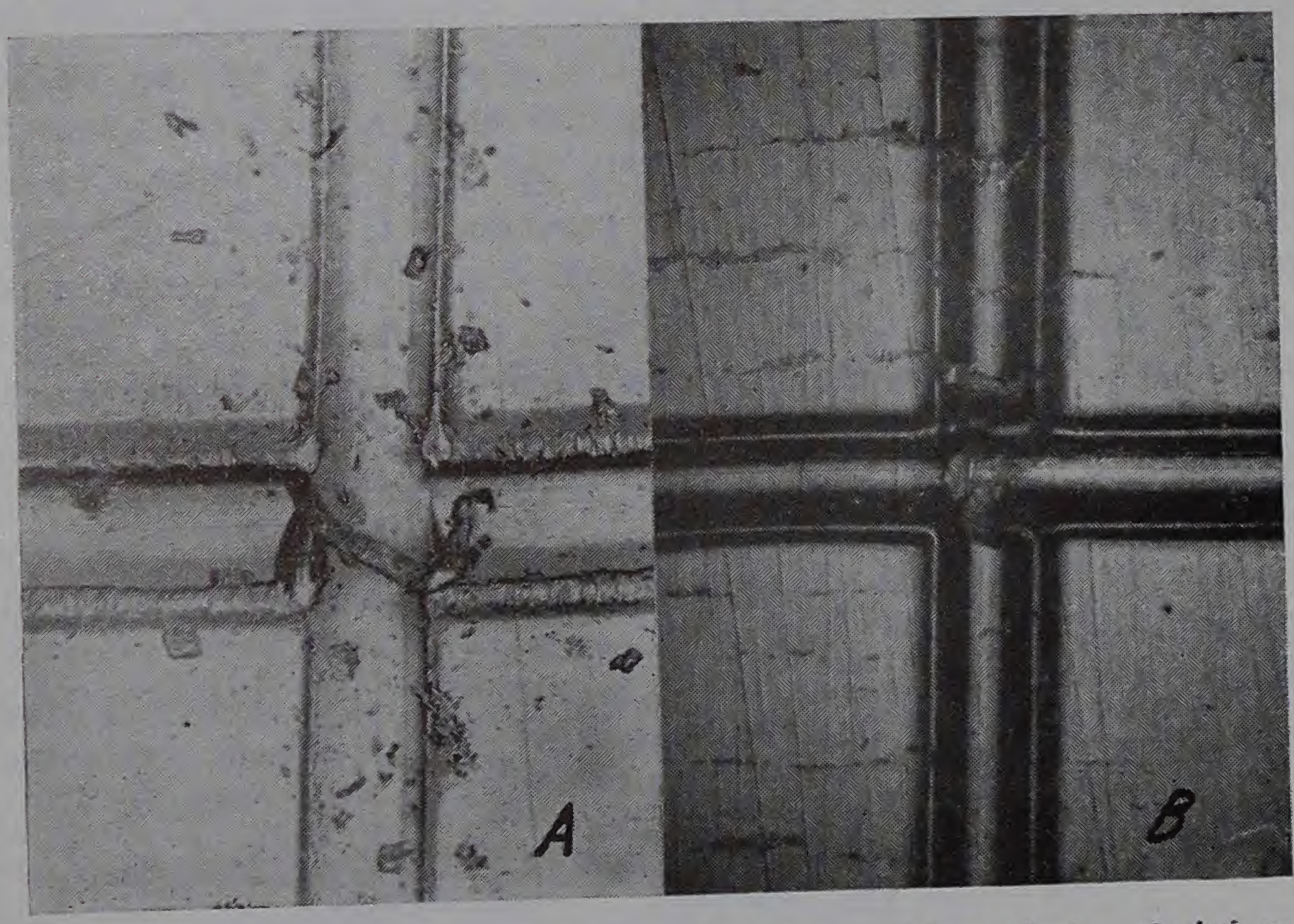

Fig. 36—Photomicrographs of scratch tests. At A is cellulose nitrate. Curled up edge indicates a scratch perpendicular to direction in which knife sliced sheet from larger slab. At B is shown a casein plastic. The fine fissures adjacent the scratches are characteristic of casein plastic (magnification—100 diameters)

Hardness Test Methods: There are various hardness test methods adaptable to different types of plastics. These are described in the following paragraphs.

1. PENETRATION TESTS: Rockwell hardness tests are most widely used to determine surface hardness of various types of plastics. Testing techniques are described in ASTM D-229; "Tests for Sheet and Plate Insulation". In order to eliminate errors due to creep, the major load is removed 7 to 8 seconds after the handle has been tripped. Readings are taken on either the M-scale or R-scale. The M-scale requires a ¼-inch ball penetrator, a minor load of 10 kg, and a major load of 100 kg. Softer materials may use the R-scale which requires a ½-inch ball penetrator, a minor load of 10 kg, a major load of 60 kg. These tests

are designed for the rigid type of plastic sheet, which should be as thick as possible (¼-inch minimum), cut from sheet stock. Rockwell reading is taken within 45 seconds after removing the major load. Typical values of hardness appear in TABLE XX.

Other hardness testers, such as the Vickers tester or Knoop indenter, possess a diamond-shaped penetrator which will also effectively compare different materials. Its advantage lies in the fact that tests can be performed upon thinner sheet stocks than those required by the ball or Rockwell penetrator.

2. PENETRATION TESTS ON NONRIGID SHEETS: The Shore durometer hardness testing instrument evaluates various rubber-like or nonrigid plastic sheet stocks. Test specimens should be at least ¼-inch thick. The instrument is described in ASTM D-676; "Indentation of Rubber by Means of the Durometer". Among other instruments employed is the Barcol hardness tester, also a small hand instrument depending upon the penetration of a small spring loaded spring. This instrument is particularly useful for quick evaluations of surface hardness of thermosetting castings or laminates. Typical Barcol hardness test results are as follows:

Melamine laminate—69
Phenolic molded part—57
Nylon—8
Polymethyl methacrylate sheet—36
Polystyrene, injection molded—29
Cellulose acetate and Saran—0

The Barcol values run somewhat parallel to the Rockwell M-Hardness tests.

3. PENETRATION TESTS ON SEMISOLIDS: Using a special calibrated needle, a load of 100 grams and a time interval of 5 seconds, the relative hardness of soft, pitch-like materials is determined. The technique is described in ASTM D-5-25; "Test for Penetration of Bituminous Materials".

4. HARDNESS OF FILMS: Hardness tests upon thin films requires much careful preparation of test specimens to insure that they lie perfectly flat and smooth. A nondestructive hardness tester, the Sward hardness rocker may be employed for the evaluation. The greater the number of rocks, the harder the surface. Typical results upon materials include: Polished steel—80 oscillations; acrylics—approximately 20 oscillations.

5. REBOUND METHODS: The scleroscope hardness testers have

not worked out too satisfactorily with plastics due to the tendency of the latter to store up energy from the bouncing ball, giving a high rebound which reflects the resiliency rather than hardness of the material.

6. SCRATCH RESISTANCE: Various tests are in the process of being explored, which would evaluate the relative hardness of the plastic surface. They depend upon a sharp calibrated diamond point drawn across the surface of the material under a fixed load.

7. ABRASION RESISTANCE: One method which has proved useful in ascertaining the abrasion resistance of plastic materials employs standard 4-inch diameter specimen disks revolving in a standard abrasive sand. The disks are mounted upon an 860-revolution-per-minute vertical motor shaft and covered to a depth of about 5 inches with 20 to 30 Ottawa sand conforming to ASTM specification C 9-26. The abrasive is kept moving and ground powder is removed by a continuous air circulating means. Loss in weight of the disk after a number of revolutions is measured and taken as an index of abrasion resistance. Under identical test conditions the wear upon the steel specimens is negligible.

Another abrasion hardness tester widely used is the Taber Hardness tester, comprising a revolving table and abrading disk. Specimen weight loss is observed after a number of revolutions.

8. MAR RESISTANCE: Another form of abrasion test, though more generally known as a mar-resistance test, depends for its comparison upon smooth, well-polished surfaces of plastics which are marred by falling abrasive compound. The method is described in ASTM D-673; "Mar Resistance of Plastics." Through a glass tube about 25 inches long, the abrasive (No. 80 carborundum) falls upon the plastic sample inclined at an angle of 45 degrees. The removal of gloss is noted after different intervals by examination through a glossmeter, constructed from a calibrated light source and photoelectric cell. Typical results obtained with this type of instrument are shown in *Fig.* 37. Data were taken from a paper by Boor*. Recent abrasion tests, using high-velocity water, have been useful in determining the service acceptability of glass-cloth laminates employed as radomes on the noses of high speed aircraft. Resistance is improved materially by a rubber-like coating.

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* Boor—*ASTM Proc.*—42, Page 927, 1942.

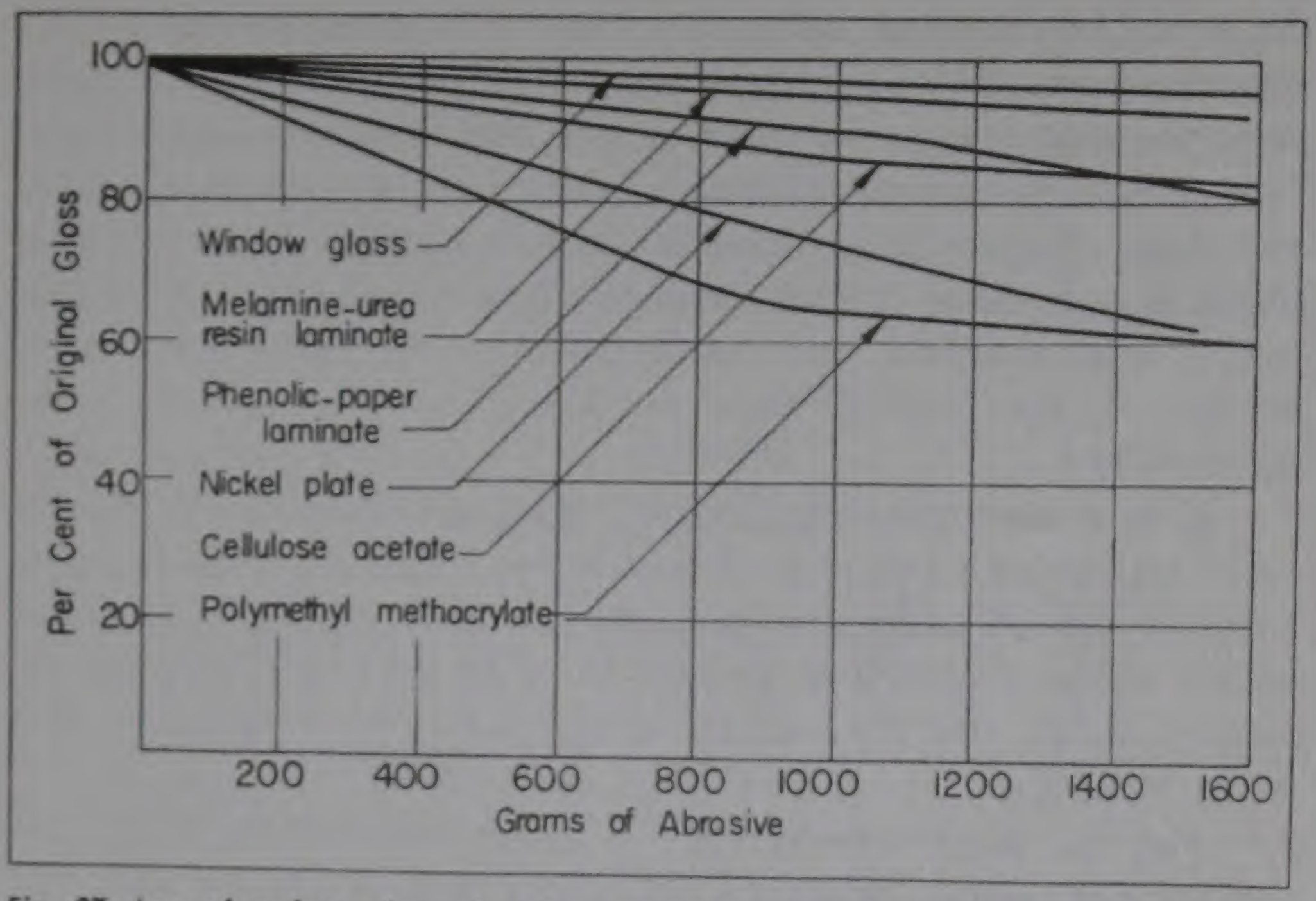

Fig. 37—Loss of surface gloss of various materials when subjected to an abrasion test used to evaluate surface hardness

Comparative evaluations of hardness testing and abrasion resistance of plastics have been reported in recent years*, though no one technique appears universally adaptable. The thermosetting melamines and molded phenolics appear generally to offer best hardness ratings, while thermoplastic acrylics and vinyls suffer the least loss in abrasion tests.

Machinability

Though machining and fabricating of plastics are discussed at length in a later chapter, comparative remarks on the machinability of plastics should appear concomitantly with discussions of physical properties. The great majority of plastics will machine well, though those with more brittle tendencies are apt to chip, detracting from the appearance. Fillers likewise influence machinability characteristics. In general, specially designed tools for plastics are recommended. Tools used for brass or cold-rolled steel stocks generally tend to run hot when working on plastics due to inability of the material to conduct frictional heat away.

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* L. Boor, J. Ryan, W. Bartoe, M. Marks. *ASTM Bulletin No.* 145, p. 68—March 1947.

As would be expected, different responses to miscellaneous tooling operations are evidenced by the numerous plastics. Molded wood-flour phenolic plastics are more brittle and must be handled carefully during prolonged machining operations to avoid breakage or splitting. On the other hand, equivalent work in laminated phenolics may be handled with much less fear of breakage. Cast phenolics, cast acrylics, and casein plastics are particularly noteworthy in this regard, their machining qualities generally being excellent.

It is necessary to perform a buffing operation on all plastics after machining to restore natural luster. This extra operation is required for all parts that normally would be displayed to public view. When a machined surface is to be concealed in some assembly, much time and labor can be saved by overlooking this extra operation.

Not all plastic materials are easily machined. There are certain composition bearings containing mineral fillers and phenolic binder which would dull the sharpened edge of tool steel after two or three cuts. This behavior may be attributed to the

TABLE XXII

Notch Sensitivity Factors of Phenolics*

Material	Notch Radius (inches)	Sensitivity Factor
Fabric-filled phenolic and polystyrene	0.025	1.0
	0.05	1.0
	0.10	1.0
	0.15	1.0
Medium-impact laminated phenolic, cloth base ..	0.025	1.3
	0.05	1.15
	0.10	1.05
	0.15	1.04
General-purpose laminated phenolic, paper base..	0.025	1.9
	0.05	1.6
	0.10	1.3
	0.15	1.2

* Flexural or tensile strengths are divided by the notch sensitivity factor for the radius involved in the notch, hole, corner, or similar type of discontinuity.

character of the filler. Special hardened-alloy or carbide-tipped tools are the only ones suited to machining of these abrasive materials. Brittle forms of pure urea plastics or solid polystyrenes are also known to be difficult to machine. Avoidance of splits and cracks in urea plastics is highly desirable even to the extent of eliminating machining operations.

Notch Sensitivity: A few comments relative to notch sensitivity may be presented at this time inasmuch as it has influence upon all of the physical properties. Most plastics display notch sensitivity to varying degrees. The effect is occasioned by an abrupt change in dimensions, sharp corners, slots, grooves, etc. Instead of lowering strength merely by the reduction of cross-sectional area, the loss in strength is much more rapid in the case of some materials. Notch sensitivity factors given in TABLE XXII are taken from a paper by Quackenbos*. They may be used as additional factors of safety when designing plastics to meet various stress conditions.

TABLE XXIII

Properties of Low-Density Cellular Plastics

Material	Density (lb/cu ft)	Ultimate Tensile Strength (psi)	Ultimate Compressive Strength (psi)
Cellulose acetate	4.1-6.3	52-103	40-110
Polystyrene	1.0-1.5	13-38	8-10
Polystyrene	5-7	111-187	121-135
Phenol formaldehyde	6.0	...	140
Phenol formaldehyde	18.0	...	1300
Buna S Rubber	4.5	72	50-80
Buna S Rubber	9	110	237
Polyvinyl formal	6-30	170	340

Physical Properties of Low-Density Plastics

Rather than include data on physical properties of low-density, expanded plastics with the other tables, a separate tabulation, TABLE XXIII, has been prepared. Considerable interest has developed in low-density, gas-expanded plastics as a core material for high strength-weight structural materials, and as sound and heat insulation. Through various casting, molding, and extrusion processes it has been possible to expand the various plastics, filling them with closed cells. For example, dissolving acetylene in styrene under pressure and polymerizing, then releasing the pressure, develops an expanded low-density structure. Other reactions, generally involving thermosetting resins, employ the activity of a highly exothermic reaction to form gas pockets and the subsequent cellular structure. However, in all cases of cel-

*H. Quackenbos—*Bakelite Review*—Vol. 18, Page 18, July, 1946.

lular materials, high physical properties and strength are not attained until the specific gravity exceeds about 0.20 or 0.25.

The properties are also dependent on the pore size in the foam, optimum properties being developed for pore sizes under 0.5 mm. Surfaces of the low-density plastics usually are protected with a relatively stiff structural member such as a glass-cloth laminate, laminated canvas, plywood, or an aluminum alloy. Good structural efficiency is obtained when the core weight is approximately 2/3rds the total weight. These combinations, called sandwich laminates, also employ resin-impregnated paper or cloth honeycomb cores with considerable success. Applications to aircraft and building trades now are current.

Chapter V

Thermal Properties of Plastic Materials

Many engineering applications of plastic materials require their utilization at subzero temperatures of −60 or −70 F and at elevated temperatures in excess of 200 F. Variations in physical properties with changes in temperature were illustrated in the preceding chapter. However, the problems become more involved when the plastics are used in conjunction with other materials possessing different coefficients of expansion and different rates of heat conductivity.

Plastics in general are good heat insulators, a characteristic which explains many of their important applications. Control knobs on electrical heating or gas-fired devices, or control wheels in sub-freezing weather are a few of the many examples which bear mute testimony to the comfortable "feel" afforded by the low thermal conductivity of plastics. In the field of heat insulation, the cellular plastics, briefly evaluated in the last chapter, compete favorably with other low-density materials serving heat insulation requirements. While the cost of the low-density plastics may be somewhat high at present for general use in the building industry, there undoubtedly are numerous specialty uses to be fulfilled by these materials. At least, if a plastic material does not comprise the substance of the insulating body, it may fulfill the function of a cement for low-density fillers.

From examination of the thermal properties, an engineer should be able to decide on the safe operating temperature for a plastic material. Thermosetting or thermoplastic classifications give good clues, but they tell only part of the story. Safe operating temperature limits will depend a good deal upon residual stresses in the plastic and the time of exposure to that temperature. Only when the conditions of application have been carefully evaluated may the correct safe working temperature be determined.

Change in physical properties at low temperatures is most apparent for nonrigid plastics, which may stiffen appreciably. Those thermoplastics which are heavily plasticized usually are the

first to show decided property differences, though in general, when flexibility is an inherent characteristic of a polymer, it shows a much less marked change at the low temperatures.

It will be noted that there are no definite softening points listed for the plastic materials in TABLE XXIV. This fact is particularly true for the high polymers which, on heating, gradually transform from a solid to a viscous semisolid body. Those resinous materials (usually natural resins or their derivatives) which possess well defined melting points generally are low in molecular weight, with a structure lacking the mechanical advantages of the higher molecular-weight polymers. However, by the time sufficiently high temperatures are reached when it may be expected to melt high polymers and pour them into molds, decomposition sets in, resulting in carbonization or degradation into lower molecular-weight fractions. Hence, forming high-molecular-weight plastics into useful articles requires not only moderate heat but also pressure, as in standard molding operations.

There are exceptions to the above requirements, in that certain high polymers such as ethylcellulose, polyvinyl chloride-ace-

TABLE XXIV

General Thermal Properties of Plastics

Material	Description	Thermal Conductivity (10^{-4} cal/sec/sq cm/deg C/cm)	Heat Distortion Temperature (deg F)	Coef. Thermal Expansion ($\times 10^{-5}$)
Phenol formaldehyde	Cast resin	3-5	104-140	5.7-15.0
Phenolic, molded	Woodflour	4-7	260-300	3.0-3.5
Phenolic, molded	Fabric filler	4-7	250-300	1.0-2.0
Phenolic, molded	Asbestos	8-16	285-325	2.12
Phenolic, laminated	Paper, Grade X	5-8	>320	1.7-2.5
Phenolic, laminated	Canvas, Grade C	5-8	>320	1.7-3.0
Urea formaldehyde, molded	Alpha cellulose	7.0	...	2.5-3.0
Melamine formaldehyde	Mineral filler	...	266	2.0-4.5
Polymethyl methacrylate	Sheet	4.0-6.0	140	7.0-9.0
Polystyrene	Molded	1.8-2.0	168-176	6.0-8.0
Polyvinyl chloride-acetate	Rigid sheet	4.0-5.0	125	7.0
Polyvinylidene chloride	Molded	2.2	150-180	19.0
Cellulose acetate	Molded (flow-286 F)	4.0-8.0	118-144	8.0-16.0
Cellulose acetate	Sheet	4.0-6.0	150-175	6.0-16.0
Cellulose acetate-butyrate	Molded (flow-286 F)	4.0-8.0	114-134	11.0-17.0
Polyethylene	Sheet	8.0	115-122	18.0
Polyamide	Molded	6.0	170	10.0
Ethyl cellulose	Molded	4.0-6.0	110-200	10.0-14.0
Cellulose nitrate	Sheet	3.1-5.1	110-150	9.0-16.0
Allyl resin (CR-39)	Cast	2.2	140-180	19.0
Steel	....	1130	....	1.1
Aluminum-24ST	....	5000	....	2.2
Brass	....	2000	....	1.8

tate, cellulose acetate-butyrate, and butyl methacrylate have been compounded into hot-melt formulations with the aid of appropriate waxes and plasticizers. The hot-melt compositions find important applications in sheet metal forming and as strip coatings for machine parts. They are described in greater detail in the chapter on casting of resins.

Thermal Conductivity

Plastic materials are good heat insulators, they conduct heat very slowly (see representative values in TABLE XXIV). From a design viewpoint, this fact is employed to advantage in reducing rate of heat transfer from a hot metal part to a part which must be handled by the bare hand or make contact with the body. Numerous molded plastic housings for fractional-horsepower motors such as are used in hand grinders or electric razors have given satisfactory performance. If the housing were made of a die-cast metal, the heat would be transferred from the electric motor to the hand so rapidly that the unit would be uncomfortable to handle. Of course, in a molded plastic housing the motor will operate at a higher temperature.

The much greater heat conductivity of the metals brings about special problems in the design of plastic and metal components which are intended to operate together. While plastics have higher coefficients of expansion than metals, mechanical failures which occur may be due to the more rapid rise in temperature of the metal, resulting in rapid expansion and the creation of excessive internal stresses. Such occurrences take place when molded plastic parts employing metal inserts are fastened to metal castings

TABLE XXV

Specific Heats of Typical Plastic Materials

(Calories per gram per degree Cent.)

Material	Specific Heat
Phenol-formaldehyde, molded	0.30-0.40
Phenol-formaldehyde, laminated	0.30-0.40
Urea formaldehyde, molded	0.40
Polyvinylidene chloride	0.32
Cellulose nitrate	0.35-0.40
Cellulose acetate	0.30-0.45
Polyethylene	0.50
Polystyrene	0.32
Polyvinyl chloride-acetate (rigid)	0.24
Methyl methacrylate	0.45
Ethyl cellulose	0.25-0.40
Steel	0.10
Aluminum	0.20

subject to considerable heat. The insert will likely expand more rapidly than the metal. While the development of metal inserts with the same coefficient of expansion as thrmosetting plastics is possible in certain aluminum alloys, the effects of sudden temperature gradients are still acute. Where temperature changes are relatively slow, articles such as special binoculars developed for the Navy have attained a high degree of precision in combinations of molded phenolics, asbestos base, with aluminum alloy inserts possessing the same expansion coefficients.

Specific Heat

In general, specific heats of most plastic materials lie between 0.30 to 0.50 (see representative values in TABLE XXV). These values may of course be substituted in appropriate formulas involving the temperature difference and the weight of the material, and calculations performed on the theoretical heat required to raise a given mass in temperature. This calculation is significant in estimating heat requirements for laminates or cast resins, though apt to be off actual values considerably because of the exothermic heat generated in certain resins which polymerize when they are being heated. Insofar as the heating of molding materials is concerned, because the mass of the plastic generally is inconsequential as compared with the mass of the mold metal, the latter is preferred for calculations. Total Theoretical Heat (BTU) = $S \times$ Weight (lb.) $\times$ Temp. Difference (deg F), where S is the specific heat.

There are considerable differences in thermal conductivity among the plastics. For example, asbestos-filled phenolics conduct heat more rapidly than wood-flour filled types, and in spite of their higher operating temperature, may be less satisfactory than wood-flour filled types which feel cooler to the touch. Molding powders have much lower thermal conductivity than the molded parts, which explains in part the necessity for closing the mold slowly. Until high-frequency preheating was developed, the oven preheating of molding compounds was a slow and inefficient process.

Various cellular plastics possess value as heat insulators, and in tests upon some of the low-density materials described in the chapter on physical properties, the K-factor was 0.25 to 0.30 for

most of the materials (Btu/sq ft/deg F/hour/inch thickness). The density of these materials is lower than various fibrous boards, loose rock wool, or felted hairs. Goggin and Bradshaw obtained some interesting results in determining the thermal conductivity of packed polystyrene fiber as a function of density (see *Fig.* 38).*

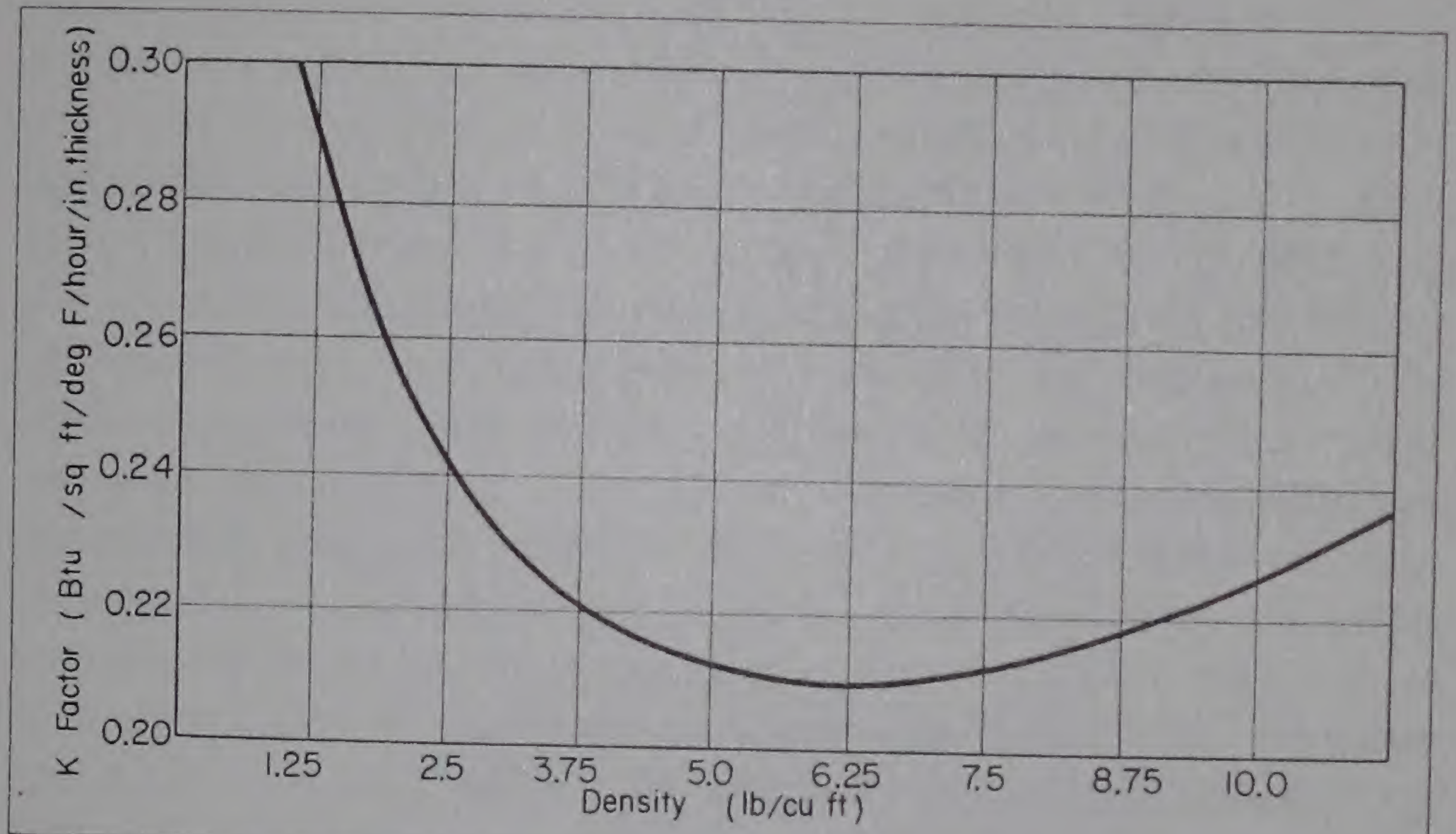

Fig. 38—Thermal conductivity of packed polystyrene fiber

Test for Thermal Conductivity—(ASTM Spec. D 325): Thermal conductivities of plastic materials are determined by comparison with known standards. If the methods outlined in the applicable ASTM specifications are observed, an accuracy of 10 per cent may be expected. A standard sheet specimen and an unknown sheet specimen are placed between two plates of uniform, but different temperatures. After steady-state conditions are obtained, the temperature gradient across the standard and the test specimen are observed. A convenient size for the specimen is 8 inches square and less than ½-inch thick. Temperature readings are made by thermocouples mounted between test specimens. Standard sheets should be of the same size as the test specimen and in thicknss one-half or not more than twice the thermal conductivity of the test specimen. Thermal conductivity of plastic materials is approximately a linear function of temperature with-

*W. Goggin and R. Bradshaw—*Mod. Plastics*—21, 101, July, 1944.

in certain limits, increasing with higher temperatures. For this reason, 70 C (158 F) is suggested arbitrarily as the temperature of the hot plate.

Thermal Expansion

In general, plastics expand two to six times more rapidly than the common metals, and in assemblies of plastics and metals, allowances must be made in the design to compensate for these differences. The compensating features should also be sufficiently broad to avoid severe stresses if the metal part should heat up before the plastic, as explained in the preceding section.

In the case of the softer, plasticized thermoplastic materials, creep under stress may alleviate some of the stress due to thermal differences of expansion with metal. The problem, however, may be occasioned by causes other than expansion differences. After or service-shrinkage, due to polymerization or evaporation of volatiles, may in fact be the prime cause of an unsatisfactory assembly of a metal and plastic component. In any event, it is good design practice to recognize that differences may exist and to avoid continuous bonding or assembly of long lengths wherever possible. Recent developments in fillers have made available special glass powders which lower the coefficient of expansion of polystyrene to 1.65 and polydichlorostyrene to 1.72 ($\times 10^{-5}$).* The density of the molded product was 1.80.

Not too much data is available on the cubical expansion of plastics, which should in most cases be the linear effect in three dimensions, except for those plastics which exhibit pronounced anistropic effects. As the temperature is raised, some materials exhibit a sharp break in expansion-versus-temperature characteristics. This discontinuity in the slope of the curves of volume plotted against temperature, known as a second order transition temperature, has been determined for several plastics**. Polystyrene has a second order transition at 81 C, polyvinyl butyral at 45 C, polymethyl methacrylate at 53 C, and polyvinyl alcohol at 58 C.

Test for Thermal Expansion: ASTM D 696—"Coefficient of Linear Thermal Expansion" is a suitable specification to follow in

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*Anon.—*Elec. Mfg.*—38, 140, Sept., 1946.

** H. Meissner and E. Merrill. *ASTM Bulletin No.* 151, p. 80, March 1948.

the determination of expansion coefficients of plastics. An acceptable range in measuring thermal expansion for plastics is −30 C to plus 30 C.

Thermal Shrinkage

Thermal shrinkage is comprised of two parts:

MOLD SHRINKAGE: Shrinkage measurement from room temperature measurements of mold to the molded article (after it has cooled down to room temperature)

AFTER SHRINKAGE: After-shrinkage or service-shrinkage is the continued shrinkage taking place in a plastic material after it has been formed. It generally is accelerated by the action of higher temperatures.

Typical mold shrinkage values for various plastic materials are listed in TABLE XXVI.

TABLE XXVI

Representative Mold Shrinkage Values

Plastic Material	Molded By	Shrinkage (in./in.)
Phenolic, woodflour filled	Compression	0.007-0.009
Phenolic, fabric filled	Compression	0.003-0.007
Phenolic, asbestos filled	Compression	0.003-0.005
Urea, alpha cellulose	Compression	0.006-0.011
Melamine, asbestos filled	Compression	0.004-0.007
Polystyrene	Injection	0.002-0.008
Polymethyl methacrylate	Injection	0.003-0.006
Cellulose acetate	Injection	0.002-0.003
Cellulose acetate-butyrate	Injection	0.002-0.003
Polyamide	Injection	0.012
Polyvinylidene chloride	Injection	0.005-0.015
Polyvinyl chloride-acetate	Injection	0.001
Ethyl cellulose	Injection	0.001-0.011

Allowances for mold shrinkage should be made in the design of molds in order to maintain reasonably accurate tolerances. Where intricate shapes are involved, however, plus nonuniform wall thicknesses, the problem of allowing for mold shrinkage becomes more difficult. This aspect is discussed at greater length in the section devoted to mold design. Molding methods also influence the results. In transfer molding, for example, mold shrinkage values may be appreciably less. This may be due in part to the higher molding pressures and the fact that the material has partly cured by the time it fills the mold.

After or service-shrinkage of thermosetting compounds may

be due largely to continued polymerization, which while only a small fraction of that incurred during molding under pressure, may bring about further dimensional changes. Typical results for a phenolic molding compound are shown in *Fig.* 39.* While the curves have leveled out after prolonged heating, if the temperature were to be raised further—say to 300 F, the shrinkage would increase another 30 to 50 per cent. Up to the present time it has not been possible to eliminate after-shrinkage in thermosetting compounds. Where a high degree of dimensional accuracy

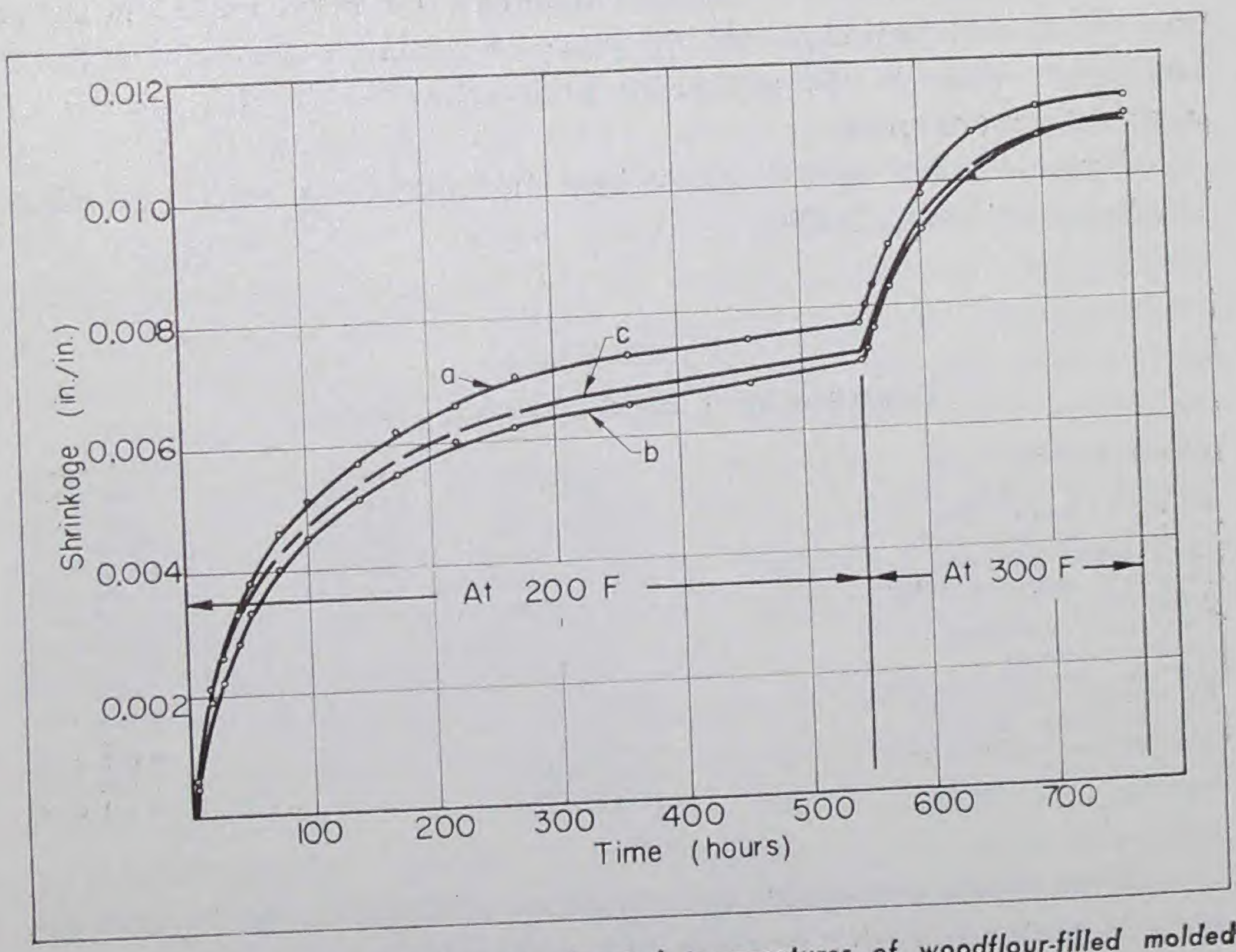

Fig. 39—Shrinkage on exposure to elevated temperatures of woodflour-filled molded phenolics.. A—one-minute cure;. B—two-minute cure;. and C—ten-minute cure

is required, however, the molder will give the molded parts an after-bake, raising the temperature slowly to as high as 250 F, where parts may be left as long as 48 hours. After this after-bake, further service shrinkage undoubtedly will be a negligible quantity at room or slightly elevated temperatures.

*J. Delmonte—*Trans. ASME*—62, Page 513, 1940.

After or service-shrinkage in thermoplastics may be quite pronounced, especially if they are heated beyond their safe limits of operation. This shrinkage generally is due to evaporation of volatiles or the relief of internal stress received during molding. For cellulose esters, the linear dimensional changes may be as much as 1 to 2 per cent (0.010 to 0.020-inch/inch) as a consequence of complete drying out (in one typical example). In the case of polystyrene held at a temperature of 212 F, shrinkage due to the relief of internal stress may be as much as 15 per cent. A more dimensionally stable compound is available in chlorinated biphenyl-polystyrene where, under the same conditions, the shrinkage is only 2 to 3 per cent, though even more satisfactory results are obtained with polydichlorostyrene.

Test for Shrinkage: ASTM D-551 "Measuring Shrinkage from Mold Dimensions of Molded Mat'l" outlines the procedure for determining mold shrinkage. Test specimen recommended is the same as used for impact and flexural tests, comprising a ½ x ½ x 5-inch bar. Molding pressures recommended are 3000 to 5000 psi and various temperatures are suggested, depending upon whether a thermoplastic, urea, or phenolic is being molded. The test molds are described in ASTM D-647 "Molds for Test Specimens of Molding Materials Used for Electrical Insulation."

Heat Distortion Temperature

The heat distortion temperature generally is recognized as a safe working temperature limit for most thermoplastics and thermosetting compounds. There are exceptions and examples which will be cited later, where higher operating temperatures have been entirely feasible, though as a good guide the values in TABLE XXIV are recommended.

Recent improvements in thermoplastic compounds have made available materials with improved heat resistance over those listed in the table. Some of these materials and their heat distortion temperatures are listed in TABLE XXVII.

The new thermoplastics with heat distortion points above 212 F open new possibilities of injection molded articles capable of withstanding the effects of boiling water. Until the last few years, this was a difficult requirement to fulfill, and a reason why many thermoplastics were kept from uses involving high temperature.

Heat Distortion Test: ASTM D-648 "Distortion Under Heat of Molded Electrical Insulating Materials" describes the testing technique for arriving at the heat distortion point of various plastics. The test specimen, ½ x ½ x 5 inches, is supported on a 4-inch span, and a load of 5.5 pounds (264 psi fiber stress) is applied at the center. The temperature is raised 1 degree C every two minutes and the temperature noted on the specimen. When the deflection reaches 0.010-inch at the center, the temperature read at that time is the heat distortion point. In effect these results measure creep under flexural loading.

TABLE XXVII

Heat Distortion Temperatures

Material	Heat Distortion Temp. (deg F)
Modified polystyrene—"Cerex"	212-230
Polydichlorostyrene	230-265
Polymethyl methacrylate—heat resisting	187-200
Polyvinyl carbazole—"Polectron"	212-300
Modified polystyrene—"Plexene M"	185-195
Modified polystyrene—"Kopper's P-8"	200-210

Useful data are obtained when the deflection measurements are made over a broad range of temperatures. *Fig.* 40, taken from a paper by Schwertz, Sauer, and Worf* illustrate the temperature stability of several representative stressed plastics, when measured on the ASTM heat distortion apparatus.

Thermoplastic Properties of Thermosetting Materials at High Temperatures

When fully cured thermosetting laminates or thermosetting phenolic molding compounds are reheated at temperatures higher than those at which they were formed, they exhibit a certain amount of thermoplasticity. This has been the basis of the post-forming operation on thermosetting laminates, described more fully in the chapter on laminates.

Some of the characteristic deformation curves are reproduced in the accompanying *Fig.* 41, taken from a paper by Delmonte and Watkins*. They indicate quite definitely that at temperatures of 400 F and higher, the thermosetting laminates can be readily

*J. Delmonte and E. Watkins—*ASTM Proc.*—1944, Vol. 44, Page 1009.
*J. Sauer, F. Schwertz and D. Worf—*Mod. Plastics*—22, 153, March, 1945.

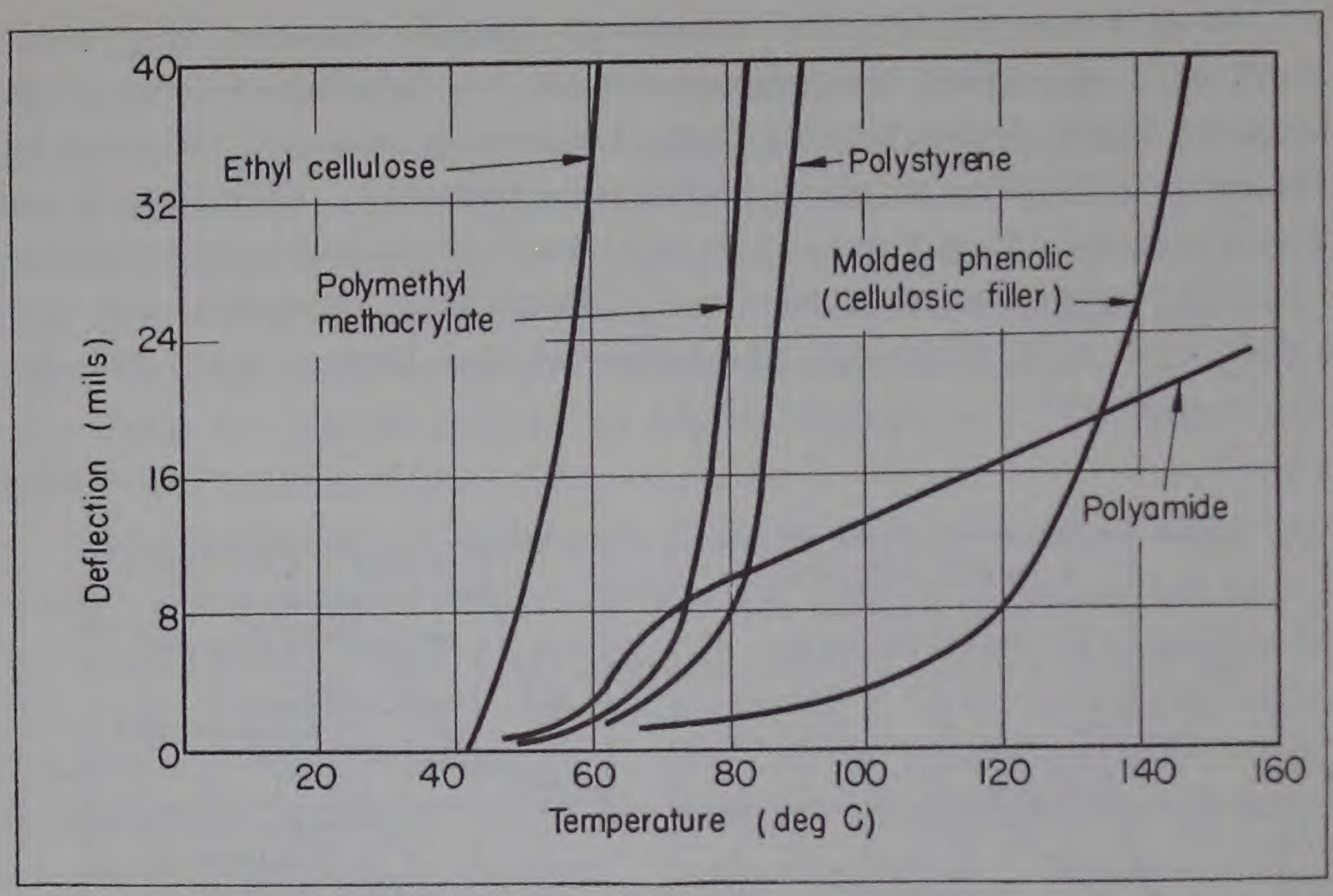

Fig. 40—Temperature-deflection characteristics of various plastics as revealed in tests on ASTM heat-distortion apparatus

formed. Other variables explored included the effect of cloth weave (greater deformation along the bïas), and the effect of cure of resin. When the resin is only partly cured, deformation definitely is greater at the higher temperatures. These results were obtained in the ASTM Heat-Distortion apparatus maintained at a constant temperature level. Physical properties are not adversely affected by this short exposure to high temperature, though if left in contact with hot oil for too long a period, blistering of laminated canvas will take place.

Maximum Safe Operating Temperature

The maximum safe operating temperature must be determined from the service conditions of the intended application. If the material is thermoplastic and is to be under some physical stress, the heat distortion point should certainly represent the maximum safe temperature of operation. On the other hand, if there is little or no stress upon the member, higher temperatures may be used. For example, the author has used molded coil bobbins of cellulose acetate at temperatures of 200 degrees F for unlimited periods with no apparent loss in serviceability of the plastics.

In the case of the thermosetting phenolic plastics, the maximum safe operating temperatures must be determined from such data as those presented for impact strength, wherein the loss in strength is illustrated after prolonged exposures. Of course if no stress is applied on the part, it may be kept at the high temperature for longer periods of time. Wood-flour phenolics, for example, are not approved for temperatures higher than 292 de-

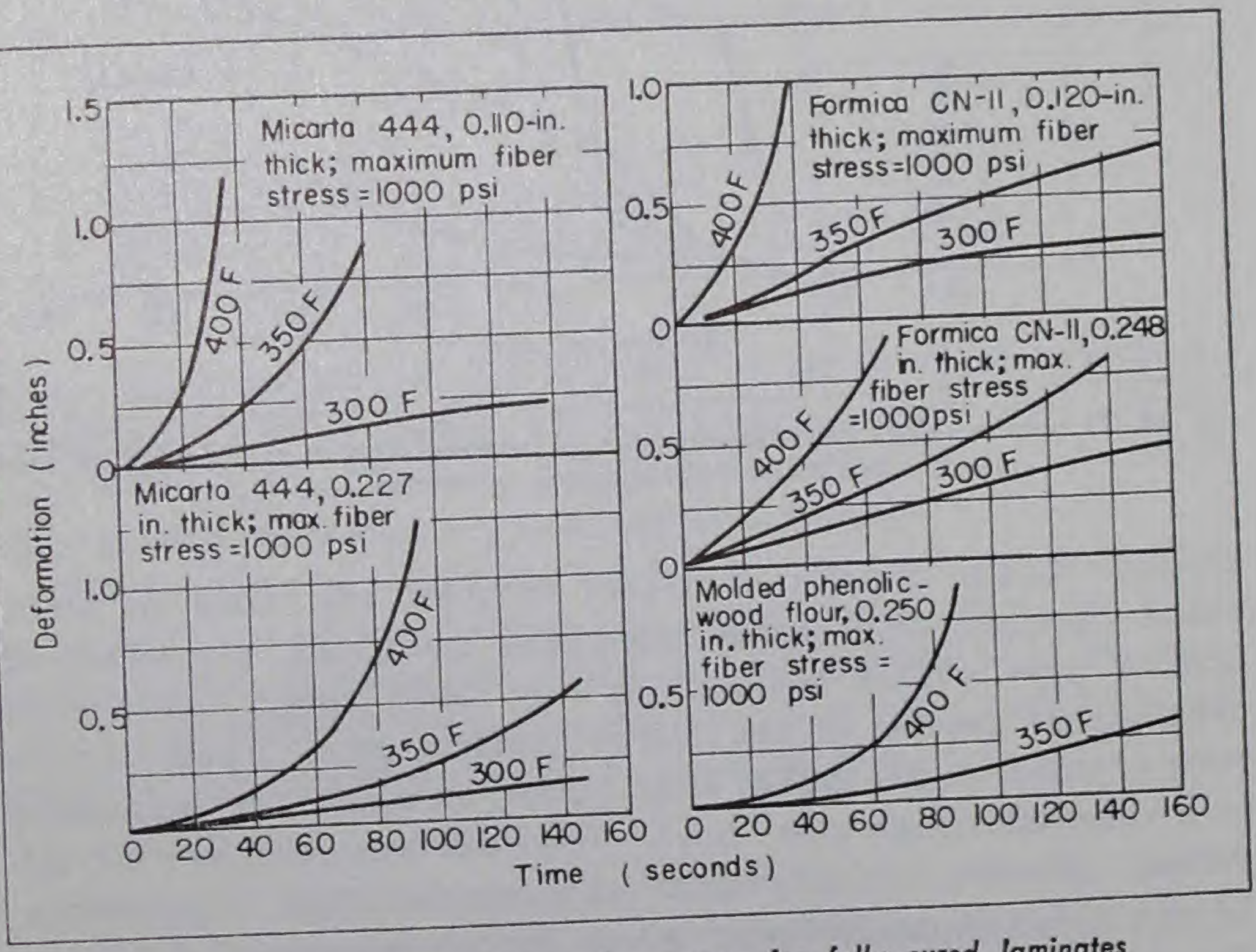

Fig. 41—Characteristic deformation curves for fully cured laminates

grees F by such agencies as the Fire Underwriters. On the other hand, asbestos compositions are formulated to withstand much higher operating temperatures indefinitely. Fabric and paper-reinforced laminated phenolics are adversely affected by prolonged exposures to temperatures above 300 degrees F. Temperatures above 400 degrees F will rapidly cause warping and blistering. Molded ureas are not recommended for operation at temperatures higher than 170 degrees F because of ensuing embrittlement.

Special molded, asbestos-base phenolic plastic materials have been developed to withstand high temperatures continuously. The only method of ascertaining the efficacy of these materials

at high temperatures is to try them out under continuous service operation at the elevated temperatures. Too often the designer has been misled by sales and advertising literature usually implying a continuous high-temperature rating for plastics which will in reality withstand these temperatures for only a short period of time. When heated continuously in excess of their ratings, these materials have slowly carbonized and deteriorated. At present, there are special grades of phenolics that will withstand 400 to 450 degrees F continuously.

A number of cold-molded plastics will withstand elevated temperatures without much difficulty. For application at higher temperatures, such as plugs for electric irons and switches for high currents, they are widely used. From an appearance standpoint, they do not have the fine luster of the phenolic resin finish, and physically they are brittle. Notwithstanding, they are suitable for many purposes.

One of the best criterions for determining how long a plastic material may be safely kept at a high temperature is to examine the change in some physical property. In this chapter the shrinkage changes accruing as a result of high temperature exposure have already been examined. Embrittlement as marked by lower flexural strength and lower impact strength is the consequence of continued exposure of cellulosic-filled phenolics at temperatures over 300 F. In the accompanying curve, *Fig.* 42, the loss in impact strength is noted with the passage of time. Under the same conditions, an asbestos-filled phenolic suffered only minor changes at 300 F.

In some recent tests upon laminated phenolics*, various grades were exposed to temperatures of 225 C for several hours. Some of the test results are shown in TABLE XXVIII. The writer in more recent tests upon phenolic laminates, has observed that the loss in strength of phenolics has depended not only on temperature, but also upon oxidation phenomena. Loss in strength in hot oil, for example, is not nearly as severe as in open air at the same temperature.

In a thorough series of tests to determine operating temperature limits of molded phenolics, Carswell, Telfair, and Haslanger reported the limits listed in TABLE XXIX, based upon a ten per cent decrease in strength after 162 hours of continuous

*E. Hausmann, A. Parkinson and G. Mains—*ASTM Symposium*—Feb. 22, 1944.

heating*. The results were reasonably close for either the flexural or impact strength, both of which were employed to evaluate the effects of temperature.

Flammability

With the exception of certain of the melamine formaldehyde compounds, most of the plastics may be ignited or caused to burst into flame. Some are immediately self-extinguishing, others will continue to burn for quite a period of time. Chlorinated resins and phosphate plasticizers in thermoplastic compositions have been

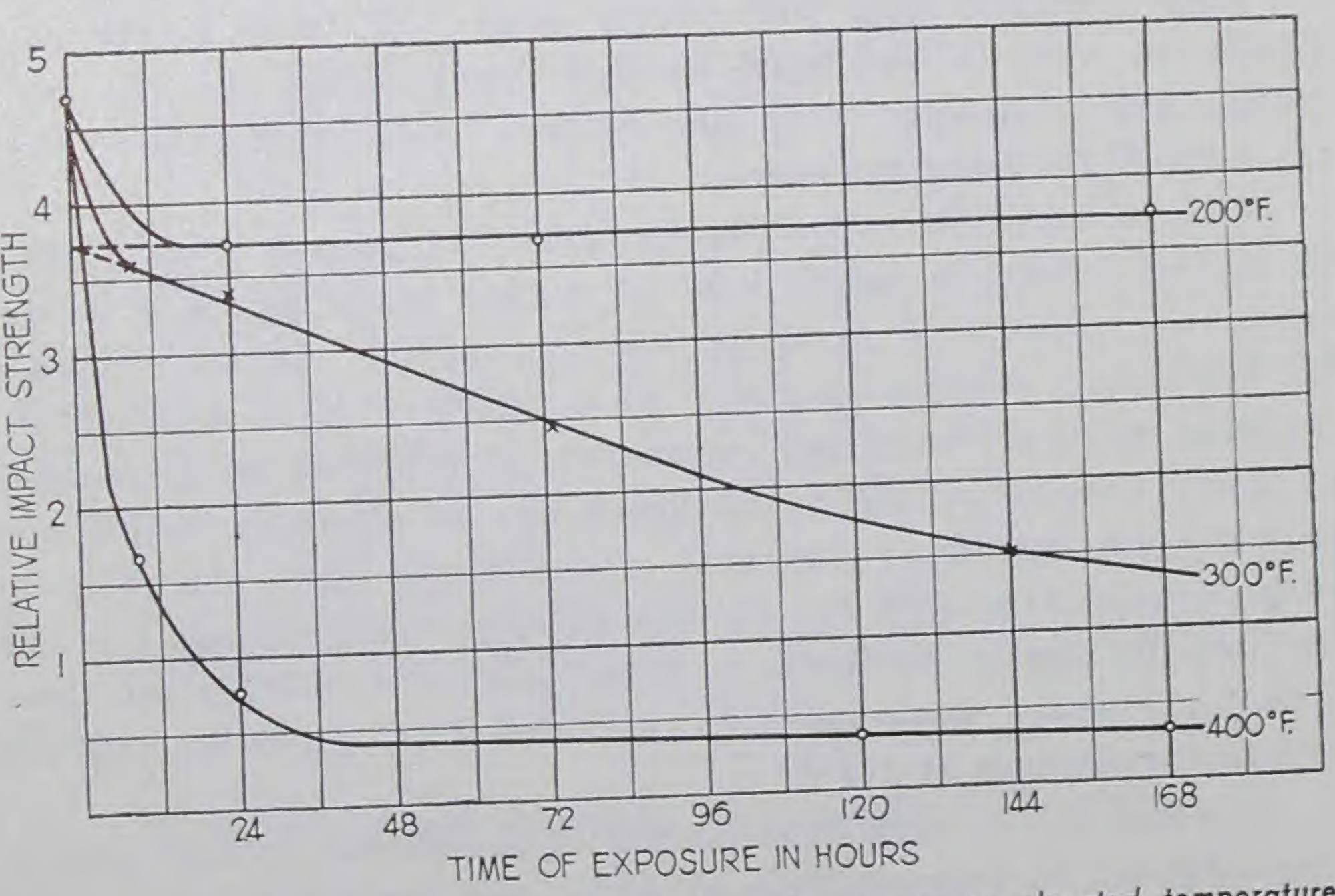

Fig. 42—Impact strength as a function of time of exposure to elevated temperatures. Tests are on Grade XX (paper-base) laminated phenolic rod, perpendicular to laminations

contributing factors toward the reduction of flammability of various compounds. Compounds such as cellulose nitrate will of course burn quite readily, though other thermoplastics are much slower in rate of burning. Self-extinguishing grades of cellulose acetate recently have been developed.

Among the thermosetting compounds, the nature and type of compound determines how it will burn when ignited. Lami-

*T. S. Carswell, D. Telfair and R. Haslanger—*Mod. Plastics*—20, 79, Feb., 1943.

nated canvas, for example, may continue to smolder after ignition due to continued burning of canvas. On the other hand, mineral-filled materials (glass or asbestos base) may experience a surface charring, though still retaïn an appreciable portion of their original strength. The cellulosic-filled phenolic compounds may be ignited at temperatures of about 400 C after approximately one minute heating time. Flame-resistant laminates were developed for use on shipboard from mineral-filled melamine-

TABLE XXVIII

Flexural Strengths of Laminates at 225 Degrees Cent.

Laminate	Initial	After 1 hour	After 2 hours	After 4 hours	After 14 hours
Phenolic, paper base	14,000	12,100	9700	10,600	7800
Phenolic, canvas base	21,000	11,300	9850	6960	3120
Phenolic, asbestos base	22,800	15,700	16,000	12,300	16,000

formaldehydes. These possessed hïgh ignition temperature, low burning time, and reasonable retention of mechanical strength after burning. Good retention of flexural strength has also been observed for phenolics reinforced with asbestos webs.*

TABLE XXIX

Limiting Temperatures* for Phenolics

Material	Limiting Temp. (deg. F) Impact	Flexural
Pure phenolic resin	284	284
Woodflour-filled phenolic	302	338
Fabric-filled phenolic	266	302
Cord-filled phenolic	266	266
Mica-filled phenolic	392	392
Asbestos-filled phenolic	428	428

* Based upon ten per cent reduction in impact or flexural strength after 162 hours of heating.

Tests for Flammability: ASTM D-568 "Flammability of Plastics 0.050-in. and under in Thickness" outlines an excellent procedure for evaluatïng the flammability of thin foils. A fusee strip of cellulose nitrate, one inch square, is stapled to the test specimen and ignited. Time of burning and area burned are reported.

ASTM D-635 "Flammability of Plastics over 0.050-in. in Thickness" outlines a procedure whereby the specimen is supported horizontally on a rïng stand and ignited with a bunsen

*J. Gale, R. Stewart and J. Alfers—*Plastics*—2, 56, June, 1945.

flame. Rate of burning is determined from an average of several tests. Another tentative method, ASTM D-757, introduces a globar heating element for igniting self-extinguishing types of plastics. Still other methods which have been employed, include a constant-temperature bath of fused salts which will ignite the plastic.

High-Temperature Resistance: It is apparent that one of the best criterions for determining the service temperature limit of plastics is the heat-distortion point. This factor considers stress as well as temperature. Considering all of the plastics as a group, however, the silicone resins and polytetrafluoroethylene appear as the only resinous materials at the time of writing capable of withstanding temperatures over 500 F. Application of a silicone rubber-like material to resistance wire coils is illustrated in *Fig.* 43. Silicones have also been utilized as insulating materials for electric motors and, in permitting much higher operating tem-

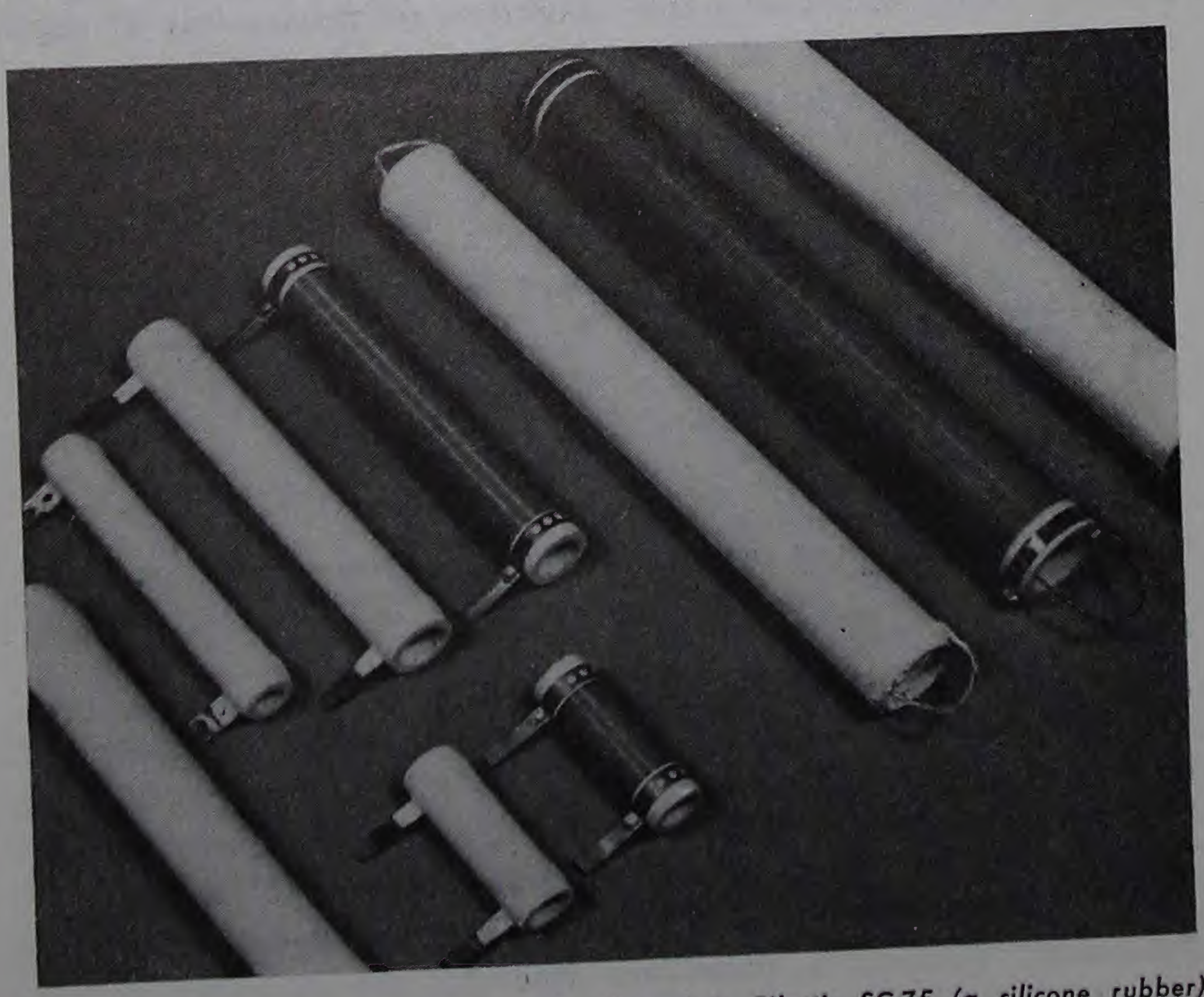

Fig. 43—These wire-wound resistor coils, dipped in Silastic SC-75 (a silicone rubber), operate at 500 F and withstand the thermal shock of being plunged nine successive times from that temperature into icy sea water

peratures than possible with the usual classes of insulating materials, will permit a much greater horsepower output for a given motor size.

Low Temperature Resistance: Polyethylene, polyisobutylene, silicones, and polytetrafluoroethylene, appear among those nonrigid plastics capable of retaining good flexibility at low temperatures. The low-temperature flexibility of polyvinyl chloride-acetate has been assisted through the selection of certain plasticizers such as dioctyl phthalate and trioctyl phthalate. An ASTM Test D-736 "Low-Temperature Brittleness of Rubber and Rubber-like Materials" has compared the nonrigid plastics at low temperatures. Test specimens are mounted in a loop and attached to plates spaced 2½ inches apart. After a suitable period of exposure to a prescribed low temperature, the plates are brought to a position where they are one inch apart. The specimens then are examined for visible cracks.

SPI Method of Classification of Molded Plastics

A classification chart for molded plastic materials has been adopted by the SPI (Society of Plastics Industry). The grade number ascribed to a plastic material consists of five digits, based upon certain of the thermal and physical properties of the material. The first two digits indicate the minimum heat distortion temperature using a flexural load of 264 psi (ASTM D-648); for

TABLE XXX

Representative SPI Designations for Molded Plastics

Material	SPI Grade Number	ASTM Heat Distortion Temp. (deg F)	ASTM Impact Strength (ft lb/in.)	ASTM Tensile Strength (psi)
Cellulose acetate (D-706-Type S-general-purpose)	11172	110	1.7	2000
Cellulose acetate (D-706-Type VH-heat resistant)	16056	160	0.5	6000
Ethyl cellulose (D-787-Type I)	14256	140	2.5	6000
Polystyrene (D-703-Type I)	17035	170	0.3	5000
Phenol-formaldehyde (D-700-Type 3)	26036	260	0.3	6000
Melamine formaldehyde (D-704-Type I)	30026	300	0.2	6000

example, 10 for 100 F, 11 for 110 F, etc. The next two digits indicate the minimum impact strength (ASTM D-256). For example, 0.03 for 0.3 ft lb, 10 for 1.0 ft lb, etc. The last digit indicates the minimum tensile strength (ASTM D-638). For example, 5 for 5000 psi, 6 for 6000 psi, etc. According to the classification, a grade number of SPI 10232 would express 100 F heat distortion temperature, 2.3 ft lb impact, and 2000 psi tensile strength. This system of classification is assuming increasing importance among designers and engineers employing molded plastic materials. A few typical examples selected from the classification chart are listed in TABLE XXX.

Chapter VI

Electrical Properties of Plastic Materials

As electrical insulating materials, plastics are outstanding for their general all-purpose utility. Aided by good mechanical strength, they are widely applied in engineering designs, fulfilling a dual role as a structural as well as electrical insulating material. It is not surprising to find that electrical equipment manufacturers were among the first to support the development of plastics, finding them indispensable to their manufacturing requirements. While fields of application of plastics have extended in many directions, the electrical industry still affords the largest outlet for plastic products.

There are inorganic materials which perform better than the organic plastics at high temperatures of operation. In particular, mica sheets and high-heat porcelain are still irreplaceable. Nevertheless, as a general insulating material possessing certain distinctive features, organic plastics are outstanding. A striking example of the versatility of molded plastics is the manufacture and application of an ignition distributor housing, *Fig.* 44. Many of these have been produced in phenolics for automobile engines, though the more arc-resisting melamine formaldehyde has been preferred for high-altitude aircraft. A complicated piece, its large production is rendered practical by plastic molding, where the electrical contacting elements are maintained in precise relationship with one another, and the necessary insulating qualities are developed.

Among the physical forms of plastic insulating materials are the following:

(a) MOLDED PARTS: These provide not only a durable material of construction, but also facilitate the assembly of many small inserts, which are integrated into an easily handled unit by molding processes. Practically all thermosetting as well as thermoplastic resins have been utilized as molded parts for electrical requirements.

(b) NONRIGID FOILS AND TUBES: Thin sheets of organic

plastics, produced by extrusion or casting, possess a uniformity of texture and quality unpossessed by their predecessors of treated papers. Thin-wall extruded tubes are also outstanding for their good flexibility, color selection, insulation properties, and oil re-

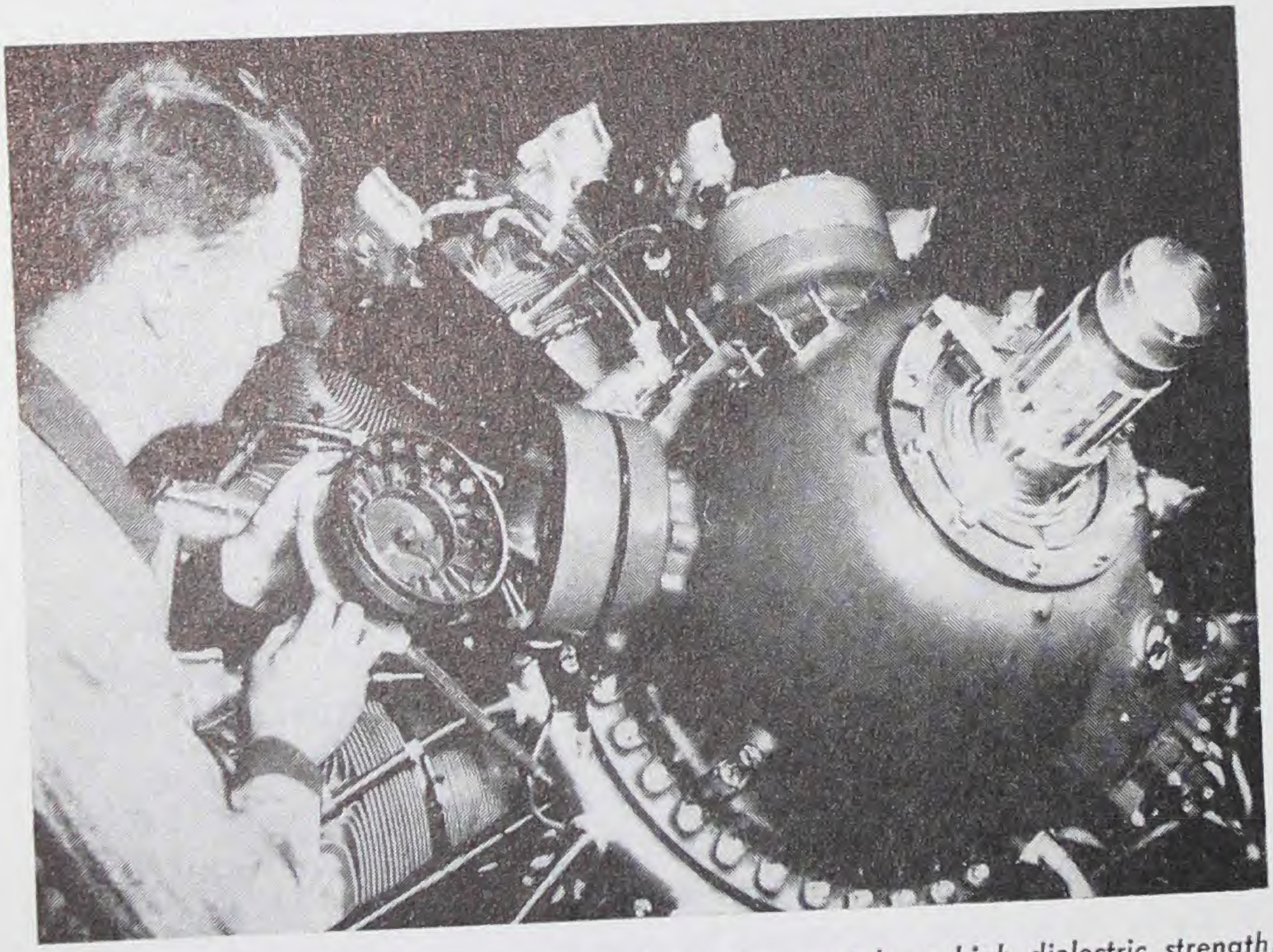

Fig. 44—Because aircraft engine ignition distributors must have high dielectric strength, arc resistance and heat resistance, they generally are molded of melamine formaldehyde

sistance. The availability of these foils and tubes has made possible a high standard of performance. Ethyl cellulose, cellulose acetate, polyethylene, polyvinyl chloride-acetate, and polystyrene are typical plastics prepared in these shapes.

(c) SHEET, PLATE, OR RIGID-TUBE INSULATION: Laminated paper or canvas-base plastics form rigid insulating elements which fulfill the requirements in a number of electrical applications. Thinner sheets are punched out into a wide assortment of insulating members such as radio tube bases, terminal strips, armature slot insulation, etc.

(d) WIRE INSULATION: Extruded or coated directly over copper wire, plasticized polyvinyl resins and polyethylene have replaced earlier enamels or rubber as insulation. In thin coatings

for magnet wires, polyvinyl formal has demonstrated a toughness and abrasion resistance unsurpassed by earlier oil-base enamels. As thick insulating sheaths, plasticized polyvinyl chloride has added permanent flexibility and resistance to oils and greases to wire insulation. Polyethylene sheaths are preferred for the ultra high frequencies.

(e) COATINGS: Many of the organic plastics are available in solution form for application as a coating material. Silicone resin varnishes, alkyd resin varnishes, polystyrene solutions, bitumen-base materials, and cellulose lacquers are but a few of the plastics applied as coatings or impregnants. The presence of volatiles has always hampered the build-up of thick insulation and the attainment of optimum properties. Recent developments in certain solvent free impregnants (such as "Fosterite") and polyester resins make possible a new technique of impregnating armature coils. Other solutions to this problem have been achieved by transfer molding of thermosetting materials about armatures or coil forms for fractional-horsepower motors, forming a rigid and permanent assembly. Continuous, integral contact of an insulation free of bubbles, insures long life for the electrical equipment.

While there are certain conditions appearing in the processing of molding materials which may adversely affect the inherent good electrical properties of a synthetic resin, there are also adverse circumstances which may arise in applying the materials. With the exception of a few fillers which inherently possess excellent dielectric qualities, the majority of the fillers, plasticizers, hardening agents, and catalysts detract in some degree from these properties of the synthetic resin or cellulose derivative. When a plastic is to be recommended for its electrical properties, care is exercised in processing the molding compound to minimize the effect of harmful ingredients. To maintain good electrical properties, the custom molder must not expose the materials to moisture, though such practices as preheating will do much to eliminate volatile matter that may adversely affect the final electrical properties.

From a design standpoint, the engineer must remember that a surface which is smoothly finished with a good gloss will have better dielectric properties than satin or machined surfaces, which enhance the possibility of entrapping moisture and dust that will

lower the dielectric properties. Further, he must investigate the limitations of the materials insofar as dielectric qualities at elevated temperatures are concerned and behavior in the vicinity of power arcs.

Dielectric Constant

The dielectric constant is a measure of the effectiveness of a material when used in a condenser. By definition, it is equal to the ratio of the capacity of a condenser with a given dielectric to the capacitance of the same condenser when air replaces the dielectric material. The dielectric constant of air is taken as unity. There are several factors which influence the dielectric constant, one of them being the frequency at which observations are made. For this reason it is the usual practice to tabulate the dielectric constant of an insulating material at 60 cycles, 1000 cycles, and 1000 kilocycles. Typical values are given in TABLE XXXI at approximately 21 degrees C (70 degrees F), with several other common dielectric materials included for comparison purposes. Dielectric constants of some of the phenol-aldehydic plastics are affected by changes in temperature. Over a temperature range of 25 to 90 degrees C (77 to 194 degrees F) some have been known to change as much as 20 per cent. In radio circuits, where all circuit parameters have a decided influence upon the operating characteristics of the circuit, variables introduced by changes in temperature are not always desirable and must be corrected by some form of adjustment. Stability of characteristics usually is a good criterion for critically tuned radio circuits. Other plastics exhibit greater stability in dielectric characteristics than the one just described. Water will also affect the dielectric characteristics in proportion to the amount absorbed by the material. In general, the dielectric constants of the phenolic plastics are increased after the materials have been immersed in water for 24 hours. Some laminated grades of phenolic plastics are compared in their behavior toward water in TABLE XXXII.

Variation in dielectric constants with frequency has considerable theoretical significance. The behavior of dielectrics is determined by the nature of polarization which an impressed field induces in them. While recent investigations point to some evi-

TABLE XXXI

Representative Dielectric Constants

Material	Description	At 60 cycles	At 1000 cycles	At 1000 Kilocycles
Phenol formaldehyde	Cast resin	20.0-30.0	12.0-15.0	7.0-8.0
Phenolic, molded	Woodflour	5.5-7.0	4.8-6.0	4.5-5.5
Phenolic, molded	Fabric filler	7.0-10.0	6.0-9.0	5.0-6.0
Phenolic, molded	Asbestos	12.0-15.0	8.0-12.0	5.0-7.0
Phenolic, molded	Mica	5.0-5.5	4.5-5.0	4.5-5.0
Phenolic, laminated	Paper, Grade X	....	....	4.5
Phenolic, laminated	Canvas, Grade C	5.0-7.0	....	4.5-6.0
Urea formaldehyde, molded	Alpha cellulose	7.0	6.4	5.8
Melamine formaldehyde, molded	Mineral filler	6.4-9.9	....	6.7
Polymethyl methacrylate	Sheet	3.4-3.6	3.2-3.4	3.0-3.2
Polystyrene	Molded	2.6	2.6	2.6
Polyvinyl chloride-acetate	Rigid sheet	3.2-3.3	3.1-3.2	3.0-3.1
Polyvinylidene chloride ..	Molded	3.0-5.0	3.0-5.0	3.0-5.0
Cellulose acetate	Molded (flow-286 F)	3.5-7.5	3.5-7.0	3.2-7.0
Cellulose acetate	Sheet	5.3-5.8	5.0-6.0	4.0-5.0
Cellulose acetate-butyrate	Molded (flow-286 F)	3.5-6.4	....	3.2-6.2
Polyethylene	Sheet	2.25-3.0	2.25-3.0	2.25-3.0
Polyamide	Molded	4.0-5.0	4.0-5.0	3.4-4.0
Ethyl cellulose	Molded	3.2-4.0	3.0-3.8	3.0-3.7
Cellulose nitrate	Sheet	6.7-7.3	....	6.2
Allyl resin (CR-39)	Cast	....	3.8	3.6
Polytetrafluoroethylene ...	Sheet	2.0	2.0	2.0

dence of dipolar rotation of long chain molecules in explaining the decrease of dielectric constant with frequency, most of the polarization phenomena of the plastic solids are due to interfacial types of polarization. Nonpolar substances like polystyrene or polyethylene suffer little change in dielectric constant with change in frequency. On the other hand, plastics with pronounced polar groups show decided changes with frequency, and appreciable dielectric loss factor.

During World War II, radomes constituted the largest product of the low-pressure laminating industry. Their chief function was to protect the radar antenna, and at the same time permit the passage of high frequency waves. It was observed that the radar range was seriously affected at the thickness of sheet stock equivalent to one-quarter of the wavelength divided by the square root of the dielectric constant, which is the equivalent quarter-wavelength thickness. Some designs proved inefficient, due to the fact that their thickness was in close proximity

TABLE XXXII

Effects of Water on Electrical Properties

Grade of Laminated Phenolic	Dielectric constant		Power factor	
	As received	After 24 hrs. in water	As received	After 24 hrs. in water
Paper (X)	4.7	5.8	.038	.043
Rag paper (XX)	4.5	4.9	.034	.036
Kraft paper (XP)	4.7	5.2	.042	.046
Asbestos (A)	6.6	8.0	.150	.200

to the ¼ wavelength. Optimum preferred thicknesses for polystyrene (dielectric constant of 2) was 0.418-in.; acrylic plastic, 0.180-in.; and polyester resin with Fiberglas reinforcement (dielectric constant of 4.0) was 0.296-in.

Tests for Dielectric Constant: ASTM D-150 "Power Factor and Dielectric Constant of Electrical Insulating Materials" outlines the procedure for the determination of the dielectric constant. Inasmuch as results are profoundly influenced by conditioning treatments, standard preconditioning as outlined in ASTM D-618 should be observed carefully. For determining the power factor and the dielectric constant of rigid laminated sheets in a direction parallel to the laminations, ASTM D-669 "Power Factor and Dielectric Constant Parallel with Laminations of Laminated Sheet and Plate Insulating Materials", describes special requirements for the preparation of test specimens. A schematic outline of the procedures used in determining dielectric constant and power factor follows:

1. TEST SPECIMENS: For molded or laminated sheet material, test specimens should be a 4 to 6-inch diameter disk or a 6-inch square with a thickness not less than 0.10-inch nor more than 0.30-inch. Tests upon rolled or molded laminated tubes should utilize specimens of sufficient length to provide a capacitance of at least 70 micro-microfarads. Before the test, specimens should be maintained at a relative humidity of 60 per cent and a temperature of 20 to 30 degrees C (68 to 86 degrees F).

2. ELECTRODES: Tin or lead foil disks, 4.5-inch diameter and 0.001 to 0.002-inch thick should be centered on each side of the test specimen. Tubes are wrapped with foil and pressed over a brass tube or bar electrical conducting member, such that wall thickness of the tube serves as a dielectric member.

3. METHOD FOR 25 TO 60-CYCLE TEST: Impedance bridge measurements are among the most useful for accurate determination of capacitance and equivalent resistance. An ideal condenser has no equivalent series resistance and no power loss. At low power frequencies these losses are small and require sensitive measuring apparatus such as a vacuum tube voltmeter. Parallel resistance and capacitance bridge and Schering bridge measurements usually are recommended. Resistance coupled amplifiers are the best suited for the measurements at low frequencies.

4. METHOD FOR 100-CYCLE TEST: Among the most reliable

harmonic free sources of 1000 cycles alternating current are tuning fork oscillators. Impedance bridges using this power source are useful in determining power factor and dielectric constants of plastic materials. The bridge may be tuned by aural indications in a pair of headphones, listening to a null sound, or observing visual meter readings.

5. METHOD FOR 100 TO 1500-KILOCYCLE TEST: Arbitrary test frequencies to select for measurement are 100 and 1000 kilocycles. A vacuum tube oscillator with low harmonics output would serve as a suitable energy source. It is important that the apparatus and measuring circuit be well shielded from external interference. Substitution methods are employed in introducing the specimen capacitor in a tuned resonance circuit, in parallel with an adjustable air capacitor. Thermocouple galvanometers are the conventional instrument for measuring resonant radio-frequency currents.

These test details for measuring power factor and dielectric constants are rather brief, and for more complete data the reader should refer to a standard text on electrical measurements.

Dielectric Strength

The dielectric strength of a plastic is the maximum potential gradient that the material can withstand without rupture. It is calculated from the breakdown voltage and the thickness of the specimen near or at the point of rupture, and is commonly expressed as volts per mil of thickness. When thin foils are ruptured, it is as if a small pin hole was made through the material, though when thicker sections experience dielectric failure the path of least resistance may prove to be an irregular path through the material. Phenolic plastics generally will leave a burned, carbonized path in the wake of the dielectric failure.

Aside from high voltage transformers, electrical equipments are not necessarily exposed to high working voltages. Common r.m.s. voltages are 110 and 220 volts, though in obtaining approval of electrical apparatus for sale, proof test voltages of 1000 plus twice the operating voltage may be applied to test the adequacy of the insulation. Where high operating voltages must be withstood by thin insulating foils, the designer must insure ade-

quate thickness of insulation to withstand the potential gradient. The dielectric strength of thin foils of organic plastics is remarkably high (see *Fig.* 45), and in applications to condensers or various coils, the limiting factor generally proves to be either the mechanical strength of the foil, which if torn, loses value as electrical insulation, or the length of the conducting path over the surface of the material.

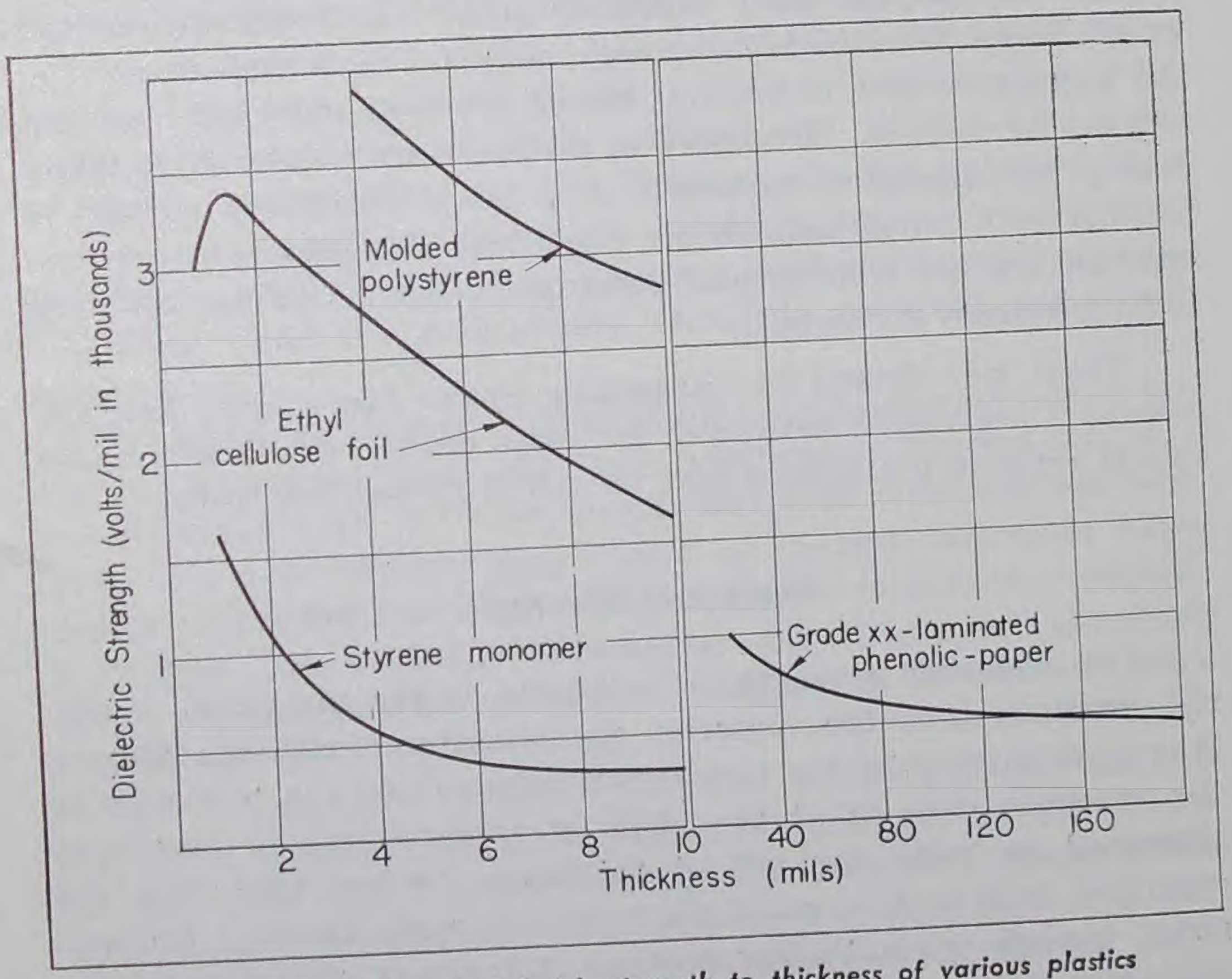

Fig. 45—Relationship of dielectric strength to thickness of various plastics

Variation of dielectric strength with thickness is quite pronounced when thicknesses of only a few mils are involved. Of theoretical interest too, is the peak in dielectric strength, in the neighborhood of 1 mil thickness. This peak has already been observed for thin films of polystyrene, shellac, and ethylcellulose. For thicknesses greater than ⅛-inch the dielectric strength decreases slightly, though not to as marked a degree as at thinner sections. The thinner the insulating foil, the more susceptible

it is to the effects of moisture, and in tests on dielectric strength, evaluations generally are made after preconditioning at some relative humidity of approximately 50 per cent.

Among other variables influencing the dielectric strength are temperature, the manufacturing process, and fillers present in the composition. The dielectric strength of organic plastics falls off at higher temperatures, a fact which is even more pronounced if there is physical stress present upon the specimen at the time the test is made. In fact the writer has obtained data showing a relationship between the physical stress in a material and its dielectric strength. Low dielectric strength sometimes is evidenced in molded articles, particularly where weld marks or flow marks are pronounced. Under the latter conditions, the dielectric strength may be a small fraction of that obtained upon a smooth, uniform section.

Among the fillers, asbestos-base materials yield the lowest values of dielectric strength. In TABLE XXXIV, the dielectric strength and other electrical properties are tabulated, and some comparisons may be made of the dielectric strengths of different materials. Comparative dielectric strengths of laminated phenolic plastics are shown in TABLE XXXIII.

In tests upon cellulose acetate, melamine-formaldehyde, phenolics, and polystyrene, Telfair and Shuster obtained data on the dielectric fatigue strength*. The fatigue limit, expressed as a percentage of the short-time dielectric strength, was in the range of 52-63 per cent for the materials tested. This establishes the value of dielectric strength below which a specimen will not fail in an indefinite time.

TABLE XXXIII

Comparative Dielectric Strengths

(A.S.T.M. 60-cycle tests on $\frac{1}{16}$-inch materials)

Material	Dielectric Strength			
	Short time		Step by step	
	25°C.	100°C.	25°C.	100°C
Paper, (X, XX)	700	500	500	350
Asbestos (A)	225	100	135	75
Light-weave fabric (LE)	500	400	300	200
Heavy-weave fabric (CE)	500	400	300	200

Tests for Dielectric Strength: ASTM D-149 "Dielectric Strength of Electrical Insulating Materials At Commercial Power

* W. Shuster and D. Telfair. *Modern Plastics*, Vol. 25, p. 123, March, 1948.

TABLE XXXIV

Electrical Properties of Plastic Materials

Material	Description	Short-time Dielectric Strength (volts/mil)	Power Factor (%) 60 cycles	Power Factor (%) 1000 cycles	Power Factor (%) 1000 kc
Phenol formaldehyde	Cast resin	75-250	25.0-50.0	20.0-30.0	9-10
Phenolic, molded	Woodflour	300-375	3.0-12.0	3-6	3-5
Phenolic, molded	Fabric filled	200-325	10.0-25.0	4-10	4-6
Phenolic, molded	Asbestos	300-350	15-35	10-25	5-10
Phenolic, molded	Mica	350-500	1-2.5	.7-1.5	.5-.9
Phenolic, laminated	Paper Grade X	400-1000	....	....	2-8
Phenolic, laminated	Fabric, Grade C	150-600	....	....	2-8
Urea formaldehyde, molded	Cellulose	300-400	3.5-10	3.5-5.5	2.7-4.0
Melamine, molded	Mineral filled	390	7-17	....	4.1
Polymethyl methacrylate	Sheet	500	5-6	5-6	2-3
Polystyrene	Molded	500-700	.006-.05	.005-.05	.01-.05
Polyvinyl chloride-acetate	Sheet	400-425	.7-1.0	1.1-1.3	1.8-1.9
Polyvinylidene chloride	Molded	350-400	3-8	3-15	3-5
Cellulose acetate	Molded (flow 286F)	250-365	1-6.0	1-6	1-10
Cellulose acetate	Sheet	275-350	2.0-2.5	2.5-4.0	4.0-6.0
Cellulose acetate-butyrate	(flow-286F)	250-400	1-4	....	1-4
Polyethylene	Sheet	400-475	.03-.05	.03-.05	.03-.05
Polyamide	Molded	350-400	1.4-5.0	2-5	4-7
Ethyl cellulose	Molded	470-550	.8-3.0	.8-1.5	1.7-3.6
Cellulose nitrate	Sheet	300-600	6-15	....	7.0-10
Allyl resin (CR-39)	Cast	568	....	1.0	6.0
Isolantite	Ceramic	300-500	....	....	.4
Fused quartz	——	....	....	....	.022

Frequencies" established two procedures for the determination of dielectric strength:

1. SHORT-TIME DIELECTRIC STRENGTH: The voltage is increased from zero to breakdown at a uniform rate. The rate of voltage application shall be 0.5 to 1.0 kv per second. This test is used most frequently for comparative results as it is conducted rapidly. A motor-operated voltage controller (such as a "Variac") in the primary of the testing transformer generally is recommended.

2. STEP BY STEP TEST: An initial voltage equal to 50 per cent of the short-time breakdown voltage is applied, and then certain increments of voltage are applied and maintained until failure occurs. The increments of voltage for molded plastics, held at each step for one minute (ASTM D-48) are as follows:

Short Time Breakdown Voltage	Increment of Increase of Test Voltage
25 kv or under	1.0 kv
25– 50 kv	2.0 kv
50–100 kv	5.0 kv
Over 100 kv	10.0 kv

The short-time test method, giving the highest values of dielectric strength, is employed most frequently. The answer is obtained readily and affords an interesting comparison between materials. A slight current leakage invariably occurs across an insulator under a potential gradient heating up the conducting path. In raising this localized temperature more leakage occurs, until dielectric breakdown eventually takes place. As may be expected, the dielectric strength is adversely affected by increasing temperatures.

Molded test specimens are 4 inches in diameter and $\frac{1}{8}$-inch thick, and the test electrodes 1 inch in diameter and 1 inch in length, with edges rounded to a radius of $\frac{1}{8}$ inch. The test specimens prepared from sheets or plates of insulating material are of sufficient area to prevent flashover under the conditions of test. The electrodes are 2 inches in diameter, with edges radiused to $\frac{1}{4}$ inch.

When arcing occurs over the surface of molded or laminated materials during test, it sometimes is recommended that tests be conducted in a good grade of insulating oil. For voltages up to 50 kilovolts, the capacity of the testing transformer

should be not less than 2 kilovolt amperes, and above 50 kilovolts, not less than 5 kilovolt amperes.

Power Factor

Of singular interest are the power factors exhibited by the various plastic materials for electrical and radio equipment. By definition, the power factor of an insulating material is the ratio of the power loss (watts) in the material to the product of the volts and amperes through a capacitor in which that material is the dielectric. The power factor is a measure of the power absorbed by an insulating material in the presence of an alternating-current field. The electrical losses, due to dielectric hysteresis, which is the result of molecular friction, creates a certain amount of heat.

An ideal condenser would have no loss in energy and zero power factor, in which case the current wave would lead the voltage wave by fully 90 degrees. This condition is practically unattainable, though fused quartz and polystyrene approach the ideal closely. Not only is the attainment of a low factor at high frequencies desirable in radio and communications apparatus, but also a power factor that will not be subject to change due to ramifications of weather, temperature, and cold flow of the material. The last feature is a disadvantage of thermoplastic materials, inasmuch as they are subject to cold flow, particularly if the surrounding temperature is raised too high. Designs must have provisions to minimize cold flow.

In radios the dielectric must possess low water absorption as the characteristics of the circuit would change on humid days should the materials be hygroscopic. Paper and fiber behave poorly in this respect, while polystyrene and polyethylene have the lowest absorption of all the resins.

Phenolic materials for radio condenser insulation in some cases have been limited, due to their comparatively high power factor and slight moisture absorbing qualities. As a result, an effort has been made to develop "low-loss" phenolic materials that will compete with other dielectrics. This has meant more careful selection of mica fillers, and removal of moisture as far as possible. Though better suited for electrical purposes than other phenolic resins, the low-loss materials are outclassed by polystyrene and polyethylene. Polystyrene in molded and lacquer

form has been of incalculable value to the industry. Low power factors mean a great deal to radio engineers, and the availability of plastics to suit requirements is another evidence of the utility of these materials. Comparative values of power factors are given in TABLE XXXIV.

Another quantity, the loss factor, often is used to compare various dielectrics. It is a direct measure of the rate of heat generation per unit volume of a material caused by the dielectric loss at a stated frequency, voltage gradient and temperature. It may be calculated from the following relation:

$$LF = K \times PF$$

where PF is the power factor, K the dielectric constant and LF the loss factor.

This formula is an approximation of the true calculation of the loss factor, which is equal to dielectric constant times the cotangent of the dielectric phase angle. The dielectric phase angle is the angular difference in electrical degrees between the sinusoidal voltage applied to the dielectric and the component of the resulting current which has the same frequency as the applied voltage. The cosine of this phase angle is the power factor. When less than 0.1 the cotangent of the phase angle and the cosine of the phase angle are substantially equal, and the two may be used interchangeably. For higher power factor (higher values of cosine of phase angle) corrections would have to be made.

Power factors and loss factors of plastic materials are dependent to an appreciable measure upon the operating temperature and moisture content. The presence of water gives a relatively high power factor at 60 cycles and 1000 cycles. Some authorities are inclined to rely upon the power factor at 60 cycles as an index of insulation quality. The loss factors of molded phenolic plastics with asbestos base are about three times that of fabric or wood-flour materials. Conducting materials like graphite and the presence of catalysts or reagents which constitute electrical conductors, are a deterrent to low power factors.

Loss factors and dielectric constants will vary with frequency to some degree (see *Fig.* 46) and decidedly with temperature. Morgan and Yager conducted a valuable group of experiments on

the electrical properties of organic compounds, and some of their data is presented herewith, showing how the characteristics of polyvinyl acetate, polyvinyl chloride, and polymethyl methacrylate vary from 10 kilocycles to 10 megacycles.* Fuoss has contributed much valuable information on the electrical properties of polyvinyl esters, and the variation of dielectric constant and loss factor with temperature are shown in *Fig.* 47. These data are taken from one of his excellent papers**. It has been shown by Debing that power factors and dielectric constants of the phenolics may be reduced by substitutions at the P-position of phenol or in the methylene bridge†.

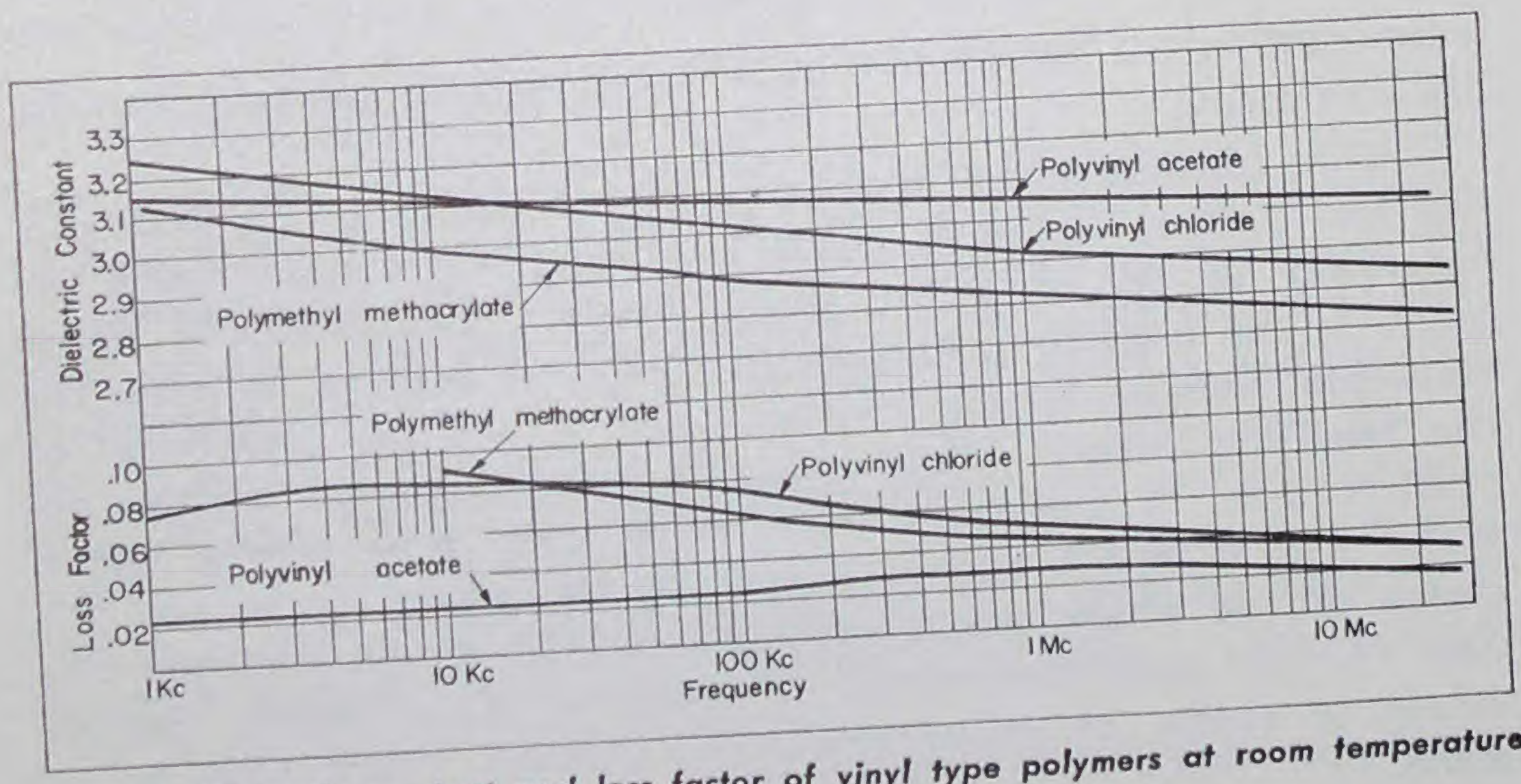

Fig. 46—Dielectric constant and loss factor of vinyl type polymers at room temperature

While most high-frequency applications of plastics to radio and electronic devices require materials with low power factors and low loss factors, limiting the choice of materials to compounds such as polystyrene, polydichlorostyrene, polyethylene, or in some cases low-loss phenolics, there are examples in which the relatively high power factor of the phenolic and melamine molding compounds is put to advantage. Reference is made to the technique of high frequency preheating of molding materials prior to placing them into the mold. High frequency preheating is de-

*S. O. Morgan and W. A. Yager—*Ind. & Eng. Chem.*—32, 1519, Nov., 1940.
**R. Fuoss—*Jl. A.C.S.*—63, 2832, 1941.
†L. Debing—*Trans. Elec. Soc.*—90, 24, 1946.

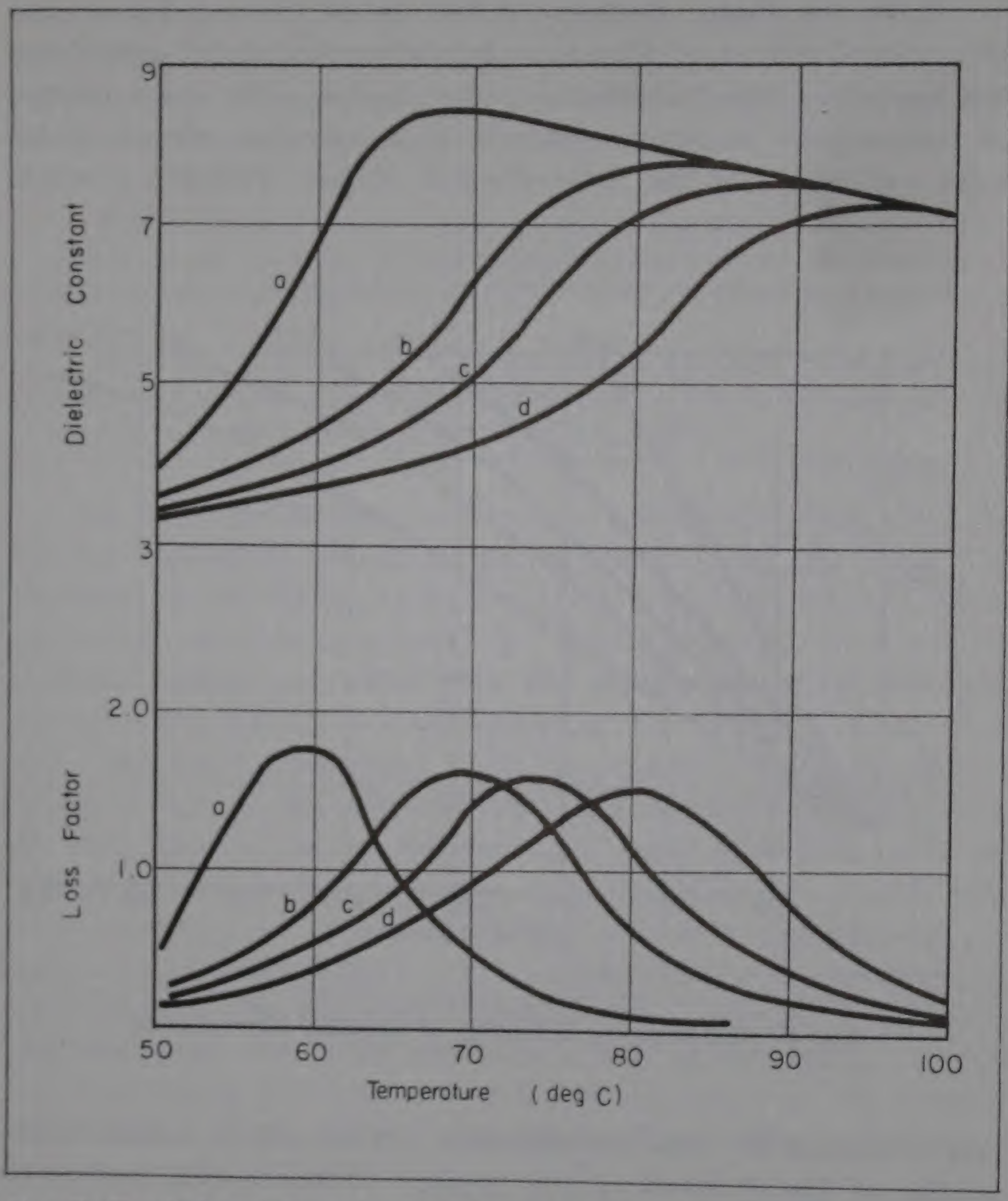

Fig. 47—Electrical properties of polyvinyl acetate (Gelva 60). a—60 cycles per sec; b—1000 cycles per sec; c—3000 cycles per sec; and d—10,000 cycles per sec

scribed more fully in a later chapter on molding operations, though the relationship of the power factor of the material is significant. For example, in *Fig.* 48 the rate of heating wood-flour filled phenolic molding compositions placed in the high frequency field is shown. While one minute may suffice by this technique to bring the materials to correct preheating temperature by the conventional art of heat transfer by conduction in an oven, 20 to 30 minutes may be required to attain the same internal temperatures.

Tests for Power Factor: ASTM D-150 "Power Factor and Dielectric Constant of Electrical Insulating Materials" establishes the procedure for determining power factor. The same bridges or susceptance variation methods in a resonant circuit which were applicable to the determination of the dielectric constant

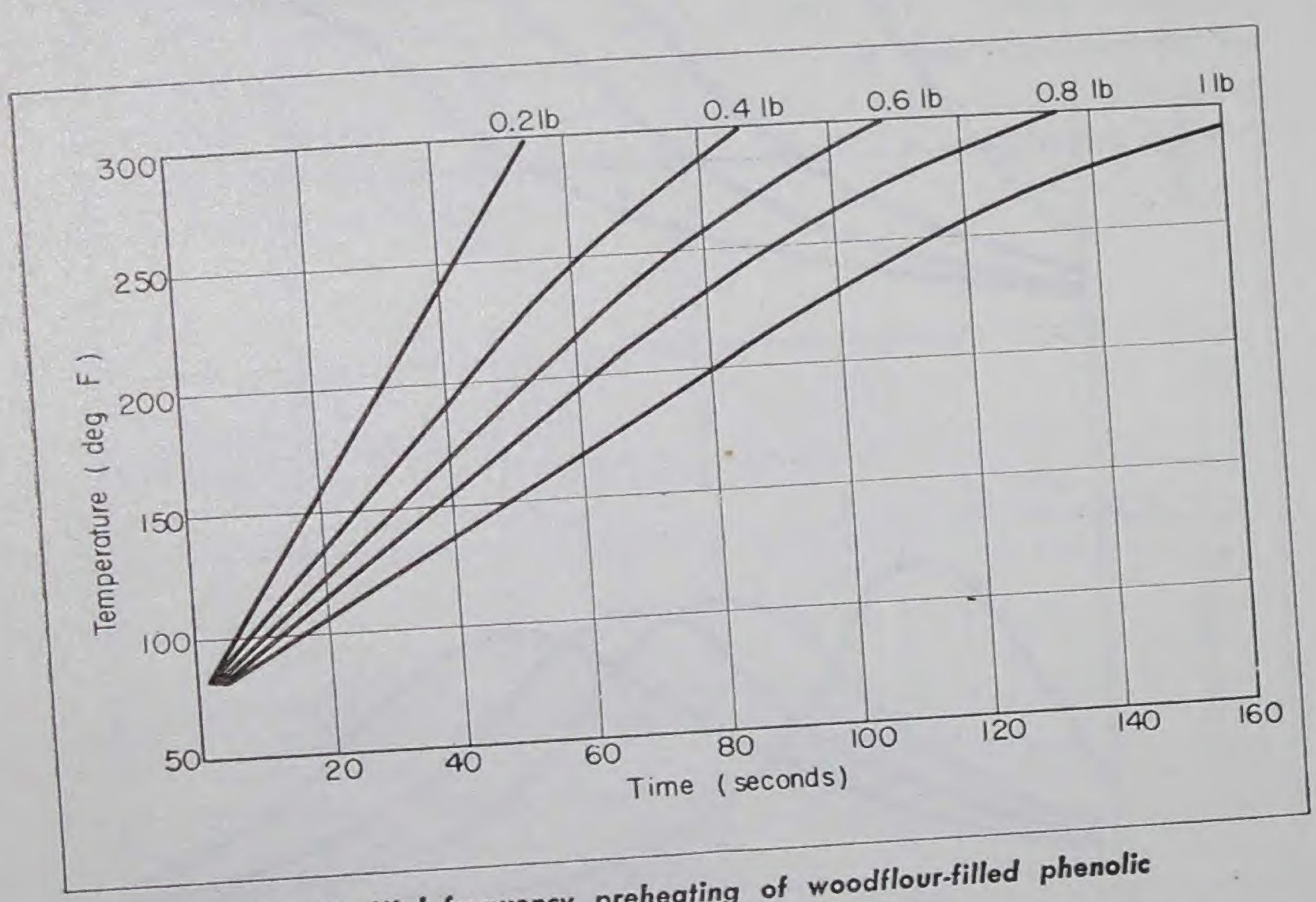

Fig. 48—High-frequency preheating of woodflour-filled phenolic

are employed for the determination of the power factor or the cosine of the dielectric phase angle. (Refer to the section on the dielectric constant for details on the specimen sizes and testing procedures.)

Insulation Resistance

Plastics, like other insulating materials, exhibit a high resistance to the passage of electrical currents. Whereas, the resistance of a good metal conductor may be of the 10^{-6} order of ohm centimeters, the resistance of a good insulator will be 10^{16} order of ohm centimeters. Such quantities are difficult to measure with a high degree of accuracy, and the variations in insula-

tion resistance over a given sample of material are usually of such magnitude as to obviate the development of more accurate instruments. Measurement may be broken down into volume and surface resistance, described as follows:

VOLUME RESISTANCE: The volume resistance between two electrodes is the ratio of the voltage applied to the electrodes to the current which flows through the volume of the insulating material.

SURFACE RESISTANCE: The surface resistance between two electrodes is the ratio of the voltage applied to the electrodes to the current which flows across the surface layers.

On some applications the surface resistivity rather than the volume resistivity proves to be the limiting factor. Dirt and moisture accumulating upon a surface will often tend to lower insulation resistance appreciably. The absorption of water by plastics, particularly those with the outside resin film removed, has seriously reduced the surface resistivity of some of the plastics. Moisture absorption, high temperatures, and presence of carbon black in the filler do not help the insulation qualities. In fact, the insulation resistance of most dielectrics falls off sharply after a certain high temperature is reached. The insulation resistance of typical insulating materials and plastics are compared in TABLE XXXV. The plastics have been measured at approximately 50 per cent humidity at a potential gradient of approximately 1000 volts per inch. It is an interesting, though not unexpected, fact that the dielectric properties of the plastics depend upon their moisture absorption. Those with least absorption are best insulators.

Volume resistivity also is dependent to a great extent upon the filler included in the molding composition. In the case of a filler such as acetylene black the molding composition may in fact be rendered semiconducting. The writer has added small amounts of this filler to standard molding compounds to render them electrically conductive, and preheated them by the passage of electrical current. This same principle has also been applied in rendering rubber compounds electrically conductive.

Surface insulation resistance of most insulators is extremely good under dry conditions, but becomes poor when exposed to damp conditions. Resistance is lowered considerably if the mois-

ture is absorbed into a continuous film, which would occur if salts from the material itself or from dirt on the surface aids the absorption. Some materials like fused quartz, have high volumetric resistivity, but low surface resistivity at high humidities.

TABLE XXXV

Volume Resistivity of Insulating Materials

(25 degrees Cent.)

Material	Ohm-Cms.
Phenol formaldehyde	10^{10}-10^{13}
Urea formaldehyde	10^{6} -10^{13}
Methyl methacrylate	$>10^{15}$
Polyvinyl chloride acetate	10^{14}
Cellulose acetate and acetate butyrate	10^{12}-10^{10}
Polystyrene	10^{17}-10^{18}
Polyethylene	10^{13}-10^{14}
Polyvinylidene chloride	10^{14}-10^{16}
Rubber	10^{15}-10^{16}
Glass	10^{16}
Fused quartz	10^{18}

Various waxes or materials like polyethylene have high volumetric as well as surface resistivity.

The electrical property most affected by moisture is insulation resistance, which decreases rapidly as foreign conducting material adheres to the surface. When any sample of plastics is placed in 100 per cent relative humidity an ionized conducting film forms quickly, and the insulation resistance drops until an equilibrium value is reached. Field determined these values for a number of plastics, listed in TABLE XXXVI.* Quite surprising is the high position of cellulose acetate-butyrate, attributed to the water lying in discontinuous pockets:

TABLE XXXVI

Effect of Moisture on Electrical Resistivity

Material	Equilibrium Surface Resistivity at 100% R.H. (ohms)
Cellulose acetate butyrate	20×10^{12}
Silicone rubber	10×10^{12}
Polytetrafluoroethylene	3.6×10^{12}
Polystyrene, sheet	8.4×10^{11}
Polydichlorostyrene	$.29 \times 10^{11}$
Ethylcellulose	$.13 \times 10^{11}$
Phenolic, mica filled	5.0×10^{9}
Glazed porcelain	3.7×10^{9}
Polyethylene	1.3×10^{9}
Phenolic laminate, Type XX	1.3×10^{9}

When high moisture conditions prevail on the surface of a plastic, the opportunity for fungi growth is enhanced, and there

*R. F. Field—Plastics & Resins—4, 9, Sept., 1945.

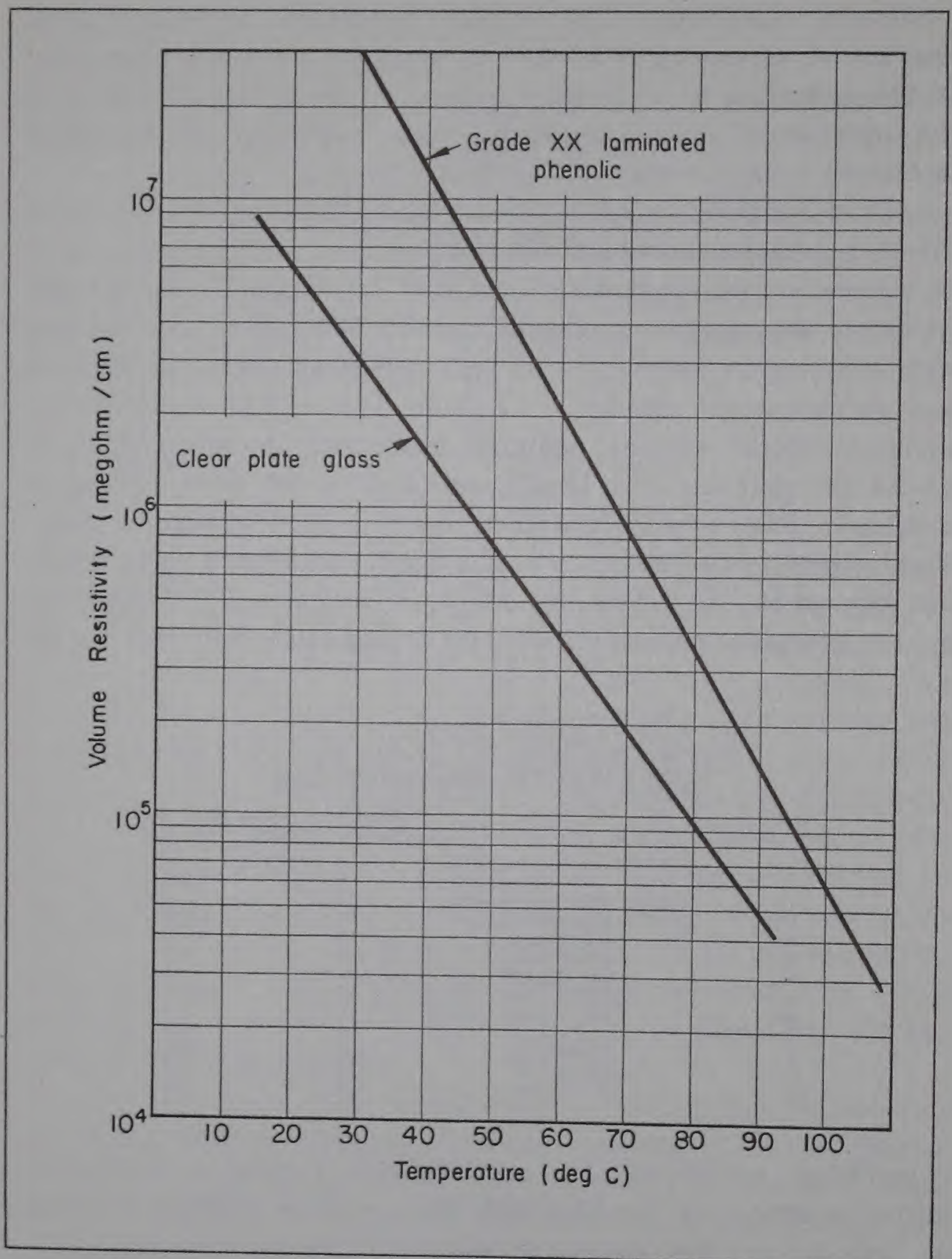

Fig. 49—Curves show how volume resistivity varies with temperature

have been numerous instances reported where this growth has developed on the surface of the plastic. The plastic itself was not affected, though the effects of the fungi growth were to lower surface insulation resistance appreciably.

No other characteristic varies as much with temperature as

volumetric resistivity. This is quite important for organic plastics which, as electrical insulation, experience a temperature rise in the operation of electrical equipment. Data which illustrates the variation of volume resistivity with temperature is illustrated in *Fig.* 49, taken from a paper by Albert**.

Tests for Insulation Resistance: The ASTM specification D-257 "Tests for Resistance of Electrical Insulation" outlines a standardized procedure for conducting resistivity tests which should be heeded by the manufacturers. One of the best methods for determining high insulation resistance is through capacitor discharge methods and galvanometer deflection. Voltage from a battery is applied across a circuit with an unknown capacitor. A universal shunt across the galvanometer is adjusted until a full scale reading is obtained. The capacitor is then shorted to discharge it fully. Test voltage is applied to capacitor again and after a certain time has elapsed the galvanometer deflection is measured. Proportioning of galvanometer deflections and elapsed time will give values

TABLE XXVII

Time Cycle for ASTM Arc Test

Current (milliamperes)	Time Cycle	Heat Generation Approx. (watts)	Total Time (seconds)
10	¼ sec. on- 1¾ sec. off	3	60
10	¼ sec. on- ¾ sec. off	6	120
10	¼ sec. on- ¼ sec. off	12	180
10	continuous	24	240
20	continuous	34	300
30	continuous	45	360
40	continuous	56	420
50	continuous	67	480
60	continuous	79	540
70	continuous	91	600
80	continuous	103	660
90	continuous	115	720
100	continuous	128	780

of insulation resistance. For low insulation resistance, a portable voltmeter connected in series with the insulation resistance across the test voltage has enough sensitivity to measure leakage currents.

Determinations of surface resistances of plastics are to be made on specimens maintained in a definite humidity for 48 hours. In the case of laminated plastics, volume resistance measurements parallel and perpendicular to the laminations should be made. Materials for electrodes are relatively unimportant, as long as

**G. Albert—*Plastics*—2, 32, June, 1945.

good contact with the insulating material is made.

There are other methods of test which evaluate the effects of low insulation resistance. These are known as leakage tests and are performed upon completed assemblies of electrical units such as motors, transformers, soldering irons, etc. After the part has been brought to operating temperature, which may also involve simultaneous exposure to high humidity, the electrical current leakage between the live or conducting part of the circuit and the frame or nonconducting portion of the motor is measured. If excessive, such that an electrical shock hazard exists, the unit is condemned.

Arc Resistance

A rather important electrical characteristic of plastics is their arc resistance. This property is significant to units such as switches or circuit breakers, when electrical current may form an arc in the immediate vicinity of the surface of the plastic. The intensity of this spark or arc depends not only upon voltage but also upon electrical current, and when the switch is slow acting (not the snap-action type of switch) the effects upon the plastic may be quite severe. In fact, those materials which behave best are those which have appreciable amounts of water adsorbed on the surface, and which are capable of delivering up copious quantities of non-ionized water vapor to quench the arc. Vulcanized fiber and shellac are two materials with good arc resistance. Their insertion into electrical molded parts such as phenolics, aid the latter in their arc resistance.

Thermoplastics such as polystyrene and acrylics possess fair arc resistance, not carbonizing in the presence of an arc, though showing a tendency to scar on the surface due to loss of volatiles formed on decomposition. On the other hand, the burned carbonized deposit formed on phenolic molded parts is definitely a handicap to good arc resistance. Urea or melamine formaldehyde molded parts on the other hand, possess good arc resistance, and are generally specified to fulfill this requirement. These plastics have been particularly serviceable on ignition distributor housings exposed to high voltages and high altitudes, a combination which causes most phenolics to arc or track badly across the surface.

Tests for Arc Resistance: ASTM D-495 "Arc Resistance of

TABLE XXXVIII

General Summary—Electrical Applications of Plastics

Typical Applications	Materials Used	Forms of Material
Thin foils for insulating purposes, as for motor or relay windings, or in condenser manufacture	Ethylcellulose Cellulose acetate Polyethylene Polystyrene	Foils 1 to 10 mils thick in various widths
Electrical wire insulation	Polyvinyl chloride Polyvinyl formal	Extruded coating, or sleeving. Dip coating, thin insulation
Impregnants for motor windings	Phenolic varnishes Silicone resins Asphaltic-base varnish	Liquid impregnants for penetrating w i n d ings, baked and dried in situ
Motor housings	Molded phenolic and urea resins	High impact - resistant materials preferred
Radio cabinets	Molded phenolic and urea resins. Cast resins and injection-molded cellulose derivatives	Attractive color assortment available in many standard materials
Insulating bushings and terminal b l o ck s for high-frequency operation	Low-loss phenolics, polystyrene and polyethylene	Molded and sheet forms
Flat insulating washers or terminal strips	Laminated phe n o l i c s, sheets and tubes	Grades of material suitable for stamping
Electrical conduit or tubing	Cellulose acetate - buty rate, ethylcellulose	Extruded tubings are held to close dimensions
Ignition distributor housings	Melamine and urea formaldehyde resins	Molded parts, usually with electrical terminals molded into the body
Housings for radar on aircraft	Polyester resins with glass cloth base	Developed into compound curves by low-pressure laminating
Storage battery cases	Hard rubber and asphaltic-base compositions	Thick-wall molded parts designed to withstand battery acids
Connecting plugs and receptacles	Molded phenolics and bitumen-base materials	Bitumen-base parts are for high temperatures
Insulation in vicinity of electric arcs. Switch parts.	Shellac, vulcanized fiber, porcelain	Molded or built-up strips
Control knobs for miscellaneous apparatus	Phenolic, urea, or thermoplastics	Colors preferred for identification purposes
Basing cements for lamps	Phenolics, ceramics	Phenolic resin adhesives
Commutator devices	Arc-resistant ureas, melamines, vulcanized fiber	Molded parts with metal strips as contact elements
Welding electrode supports	Heat-resistant and shock-resistant phenolics	Molded w i t h suitable hand grips

Solid Electrical Insulating Materials" classifies insulating materials in the following manner, according to the test methods described hereafter·

Type of Material	Arc Resistance
Hot molded or laminated materials (general)	30 secs. or under
Hot molded or laminated—high arc resist	60-180 seconds
Cold molded materials (non-refractory)	60-300 seconds
Cold molded materials (refractory)	240-480 seconds
Special materials (porcelain, slate fused quartz) ..	420-660 seconds

A high-voltage, low-current a-c arc drawn between two tungsten pointed electrodes upon the material under test, is increased at 1-minute intervals until the material fails by becoming conducting. The sequence of one-minute electrical current steps are listed in TABLE XXXVII.

In analyses of electrical applications of plastic materials, TABLE XXXVIII* will prove quite informative as to the scope of the many materials.

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*J. Delmonte—*Machine Design*—18, 116, July, 1946.

Chapter VII

Chemical Properties of Plastics

As a group, organic plastics possess a high degree of resistance to a large number of chemicals. While there are specific solvents for the majority of plastics, there are certain types outstanding in resistance to the effects of all solvents and types outstanding in resistance to acids and alkalies. The engineer familiar with the behavior of plastics in the presence of chemicals will find that many new possibilities of employing the materials in chemical processing equipments will appear.

Studies on the effects of solvents upon plastics are also of fundamental importance to many fields which use plastics in the form of thin films. Surface coatings, impregnating agents, and adhesives are but a few of the industries dependent upon solutions of plastics. This chapter makes no pretense of attempting to cover these fields, problems of which are of a specialized nature and beyond the scope of the immediate subject. However, relationships which do exist will be pointed out wherever they appear to be expedient.

Temperature effects are also pronounced, higher temperatures generally increasing the activity of the dissolving medium or the attack of the corrosive agent. In fact some materials may be relatively unaffected at low temperatures, but near the boiling point are apt to fail rapidly. Chemical activity may be latent in some plastics until exposed to the actinic rays of sunlight. A section devoted to the effects of sunlight will be presented. Under these conditions small traces of impurities may be catalyzed by sunlight, leading to unexpected results.

In the field of nonrigid plastics, the rubber-like elastomers offer qualities never before possessed by natural rubber. Resistance to oil and greases, good color selection, and permanent flexibility are assets which have established plastics in important applications. In *Fig.* 50 a typical assembly of flexible, plastic conduit (polyvinyl alcohol) is illustrated, designed to handle a variety of gases and fluids on this sealing machine. Permanent flexibility is quite an optimistic claim, but one has only to examine

the flexibility of a nonrigid polyvinyl ester after several years service and compare it with natural rubber to gain the full import of this statement.

Effects of Water

In considering the effects of water upon organic plastics, two approaches will be explored: The effects of continuous immersion in water and the effects of water vapor. Those plastics which have the lowest water absorption do not necessarily have the greatest resistance to permeation of water vapor. The absorption of water by plastics varies from complete dissolution on one hand, to excellent resistance on the other. High polymers such as methyl cellulose, sodium carboxy methyl cellulose, hydroxy ethyl cellulose, polyvinyl methyl ether, sodium alginate, and certain types of polyvinyl alcohol are completely dissolved by water.

These polymers prove useful as sizing, adhesives, and thickening agents. Partially polymerized resin polymers of urea for-

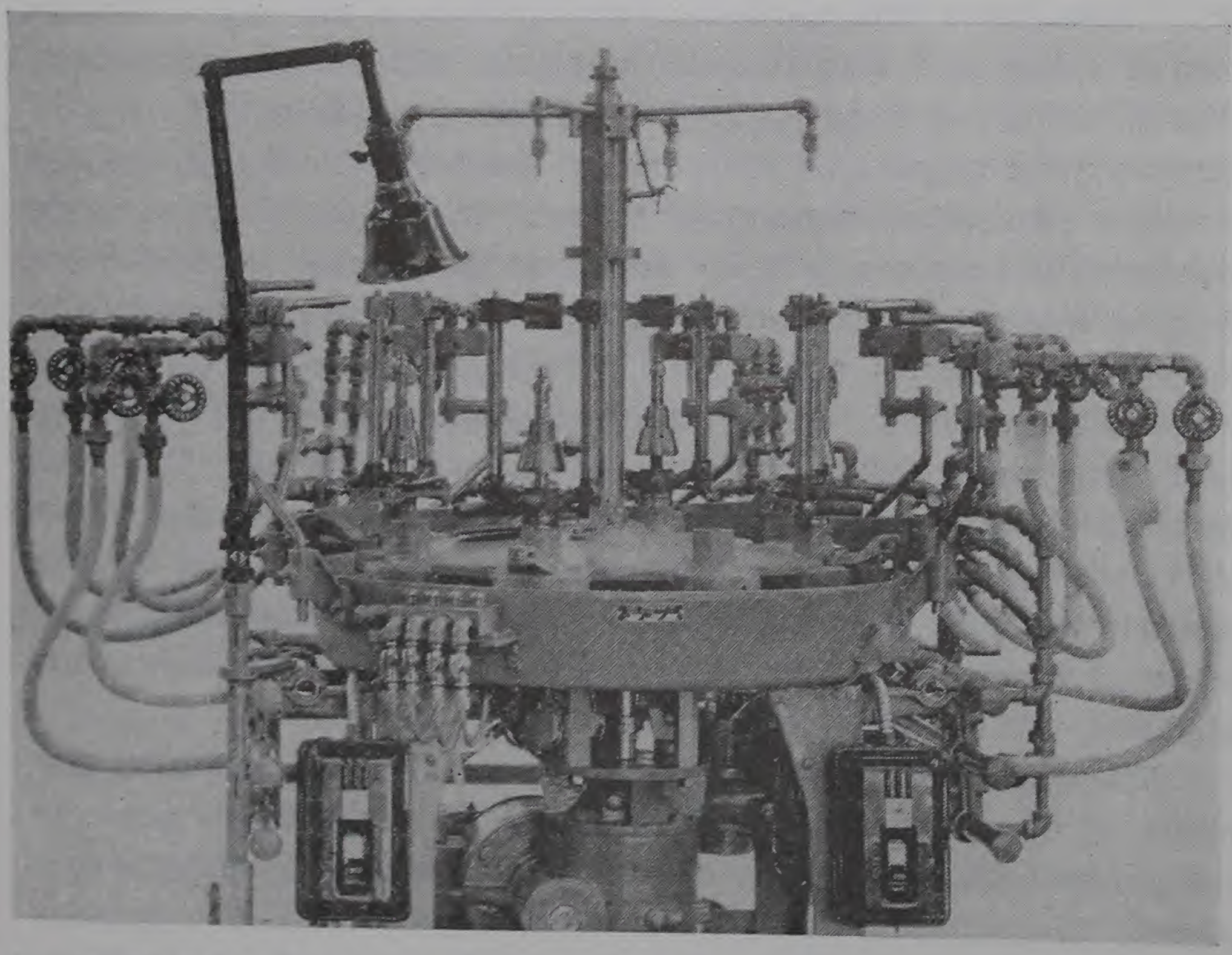


Fig. 50—Flexible lines of polyvinyl alcohol plastic carry oxygen, air and other gases to the burners of this sealing-in machine

maldehyde, or melamine formaldehyde generally are dissolved in water before application to laminates, though after proper curing attain insolubility in water. Among those plastics seriously affected by water are the protein plastics, which absorb relatively large amounts in a short time. When the proteins are treated with formaldehyde this water absorption is appreciably decreased.

While the absorption of small quantities of water does not seriously affect the appearance of the plastic, other properties may be influenced to a pronounced degree. Some of the more serious consequences of water absorption are tabulated herewith:

1. Physical properties of some plastics become lower in strength values
2. The swelling accompanying the absorption of water may be of sufficient magnitude to cause the plastic part to exceed allowable tolerances and poor fits may occur. If the absorption of water takes place unevenly over the surface of the plastic, warping will take place
3. Dielectric properties of the plastic generally are adversely affected by the absorption of water.

There are a few specialized circumstances where the absorption of water on the surface of the plastic will work to advantage. Water-lubricated laminated phenolic bearings find this characteristic quite helpful, as they depend for lubrication upon the absorption of a small amount of water. In a later chapter, these nonmetallic bearings will be described in greater detail. Nonfogging lenses for gas masks or similar articles are prepared from transparent plastics which have a high degree of water absorption on the surface. In fact saponified surfaces of cellulose acetate give good performance under these conditions. Why the lenses are nonfogging may be understood when it is pointed out that fogging is due to the formation of small globules of condensed water on the surface (as on a glass of cold water). A material which will absorb this moisture into a continuous saturated film, will eliminate the fogging.

Electrical and radio engineers are much concerned with stability of circuit constants as this is a prerequisite to accurate tuning methods. Insulation characteristics subject to change, say, due to increased humidity, are undesirable. In a like manner materials and parts that will warp under normal atmospheres are not wanted, as relative spacings of component parts are not

only important from a mechanical point of view, but also from an electrical standpoint. Consequently, with this thought in mind, engineers may have been hesitant in specifying plastics to their full utility except for decorative purposes and control knobs, because of the uncertainty of moisture absorption characteristics. Where normal broadcast frequencies are employed, a number of molded phenolic, low-loss parts, are used on tube bases, terminal strips, supports, etc. These disappear from the design, as higher frequencies are brought into play. In the latter, polystyrene and polyethylene have been applied extensively. One notable example is in the co-axial cable, for high-frequency transmission, employing low-loss plastics for conductor insulation.

One of the most complete reports on the absorption of water by plastics was presented by Kline, Martin, and Crouse*, who conducted the investigation over a two-year period. Most of the plastics continued to absorb water at a substantial rate during the first six months. Some of the results of their investigation are shown in the accompanying *Fig.* 51.

For short-time data on the absorption of water by plastics materials see TABLE XXXIX, which gives the standard ASTM water-absorption values after a 48-hour period. These are determined by changes in the weight of a standard size specimen. In order to avoid obtaining an erroneous figure for the amount of water absorbed by plastics containing water-soluble ingredients, reconditioning the specimens after immersion to a substantially dry weight is recommended. From the last figure, the true water absorption may be calculated.

Not only does the nature of the filler in the molding composition, and the nature of the reinforcing layers in laminated structures influence the amount of water absorbed, but also the method of applying the binding resin. For cellulosic fillers, the higher the resin content, the lower the water absorption tends to be. This point generally is recognized, but a factor often overlooked is that the better the penetration of the resin into the filler, rather than adsorption on the surface, the lower will be the water absorption. This has been observed particularly in the manufacture of resin-impregnated wood veneers which are bonded into high-density, strong structures. However, the better the resin penetration, the greater the degree to which the impact strength

*G. M. Kline, A. R. Martin and W. A. Crouse—*Proc. ASTM*—40, 1273, 1940.

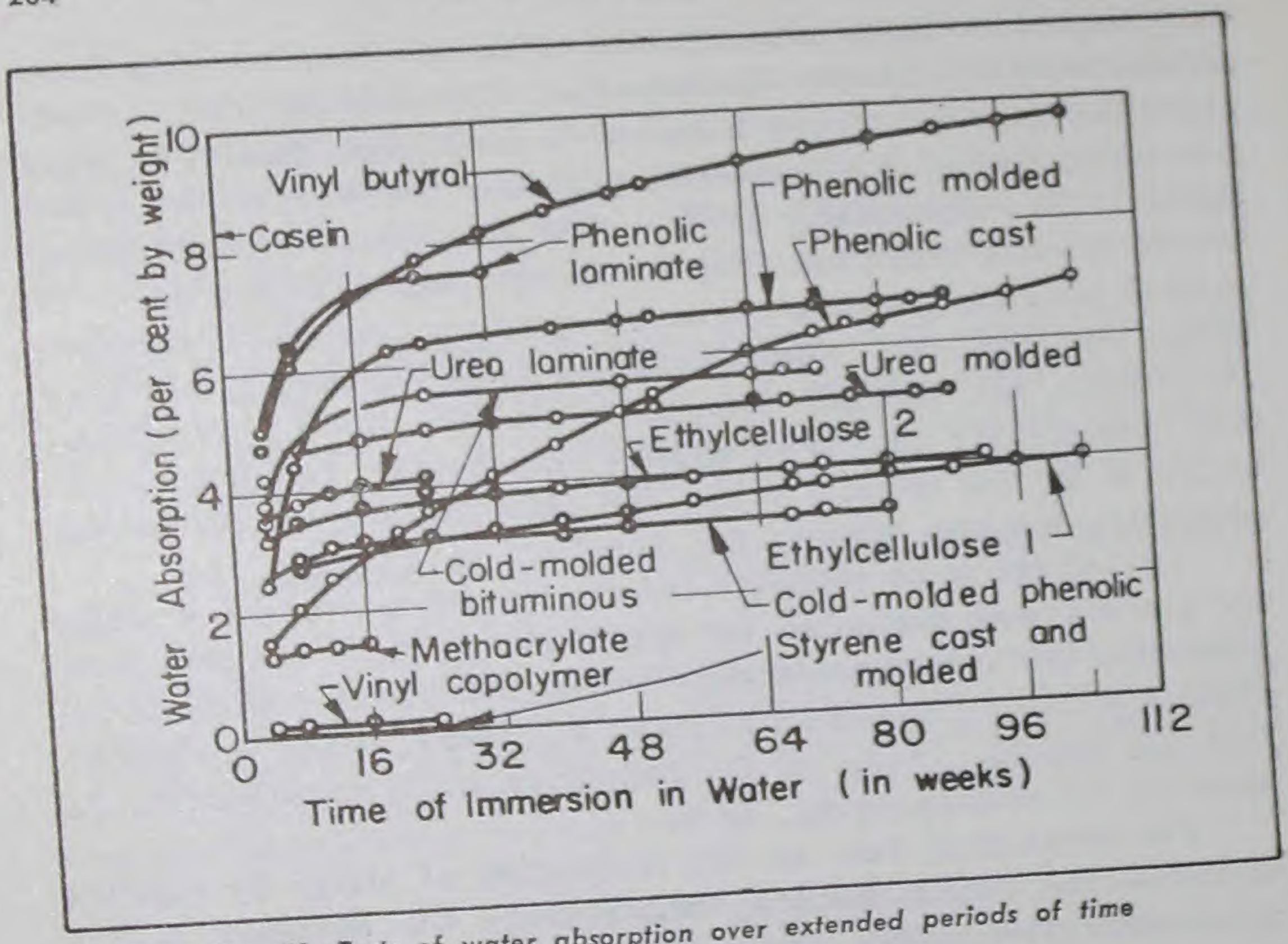


Fig. 51—Tests of water absorption over extended periods of time

is affected. In TABLE XL are given water absorption values for typical laminated phenolics, with increasing resin content from X to XXX.

TABLE XL

Water Absorption Rates for Some Laminated Phenolics

Base	Grade	Water Absorption (Per cent in 24 hours)
Paper	Grade X	4.0
Paper	Grade XX	1.3
Paper	Grade XXX	1.0
Paper	Grade C	3.0
Canvas		

It was pointed out before that even more significant than the weight change in a plastic was the dimensional change, inasmuch as this influenced the success of the application where close tolerances and fits were required. Abstracting again from the paper of Kline, Martin, and Crouse, TABLE XLI indicates the percentage dimensional changes in some of the more common plastics after different intervals of time. In examining this data, it is im-

TABLE XXXIX

Behavior of Plastics on Exposure to Water and Light

Material	Water absorption (per cent in 48 hours)	Exposure to Ultraviolet light	Aging Characteristics
Phenol formaldehyde			
molded	.1 to 1	Satisfactory	Good
molded colors	.....	Light colors fade	.....
laminated	.5 to 5	Satisfactory	Good
Urea formaldehyde, molded	.1 to 2	Satisfactory, including colors	Fair (tendency to check under some conditions)
Melamine formaldehyde, molded	.5	Satisfactory including colors	Good
Cellulose nitrate, sheet	1.4	Yellows	Warping and embrittlement
Cellulose acetate, molded	3.5	Slight discoloration	Warp in thin sections
Cellulose acetate-butyrate	1.5	Slight discoloration	Warp in thin sections
Polyethylene	.03	Satisfactory	Good
Polyamide	2.5	Slight discoloration	Good
Polystyrene, molded	.055	Yellows	Slight crazing
Methyl methacrylate	.46	Satisfactory	Slight crazing
Polyvinyl chloride-acetate	.07	Discoloration	Embrittlement (slight)
Ethyl cellulose	1.2	Slight discoloration	Slight shrinkage
Cold-molded bitumen plastic	1	Some grades turn gray	Negligible change in physical properties
Casein	13	Light colors fade and surface checks	Appearance and properties affected

portant to remember that 1 per cent change is equivalent to a change of 0.010-inch in one inch (a greater change than mold shrinkage for most materials).

TABLE XLI

Dimensional Changes in Plastics Upon Immersion in Water

Material	Per cent Change in Length After 48 hours	After 8 weeks	After 2 years
Molded phenol formaldehyde	0.05	0.65	1.35
Cast phenol formaldehyde	0.07	0.36	2.08
Laminated phenolic	zero	0.16	0.13
Urea formaldehyde, molded	0.12	1.15	2.05
Polymethyl methacrylate	0.12	0.40	0.30
Polystyrene, molded	0.13	0.25	0.45
Cellulose acetate	0.71	0.40	0.53
Casein	1.98	13.24	...
Cold molded bitumen	0.08	0.35	1.21

Changes in weight and dimensions are brought about not only by immersion in water, but also by exposure to high humidities. If the material absorbs an appreciable amount of water it may distort quite badly. This is observed particularly with thin insulating foils where sheets of regenerated cellulose or certain grades of cellulose acetate will wrinkle quite badly at high humidities. In *Fig.* 52 are given data on moisture content of 10-mil thick sheets of cellulose acetate, cellulose nitrate, and wood cellulose at different humidities. Results were obtained after 8 days conditioning at the stated humidity.

Diffusion of Water Vapor Through Plastics: Still another aspect of the effect of water upon plastics is the diffusion of water vapor through thin sheets of the material. Wrapping foils for packaging materials and foodstuffs depend a good deal upon resistance to diffusion in order to protect their contents. Comparisons generally are based upon establishing a high moisture gradient by exposing one side of the test material to a dry, dessicated container, and the other side to a specified high humidity. Deeg and Frosch obtained much useful data in a recent publication*. Their diffusion constant is determined from

$$D = \frac{NX}{23.5AT}$$

*G. Deeg, Jr. and C. J. Frosch—*Mod. Plastics*—22, 155, Nov., 1944.

where t = time in hours
X = thickness in centimeters
A = area in square centimeters
N = grams of water diffused through
D = diffusion constant

Among materials possessing excellent resistance to water vapor permeation, and not shown in TABLE XLII are films of polyvinylidene chloride and rubber hydrochloride.

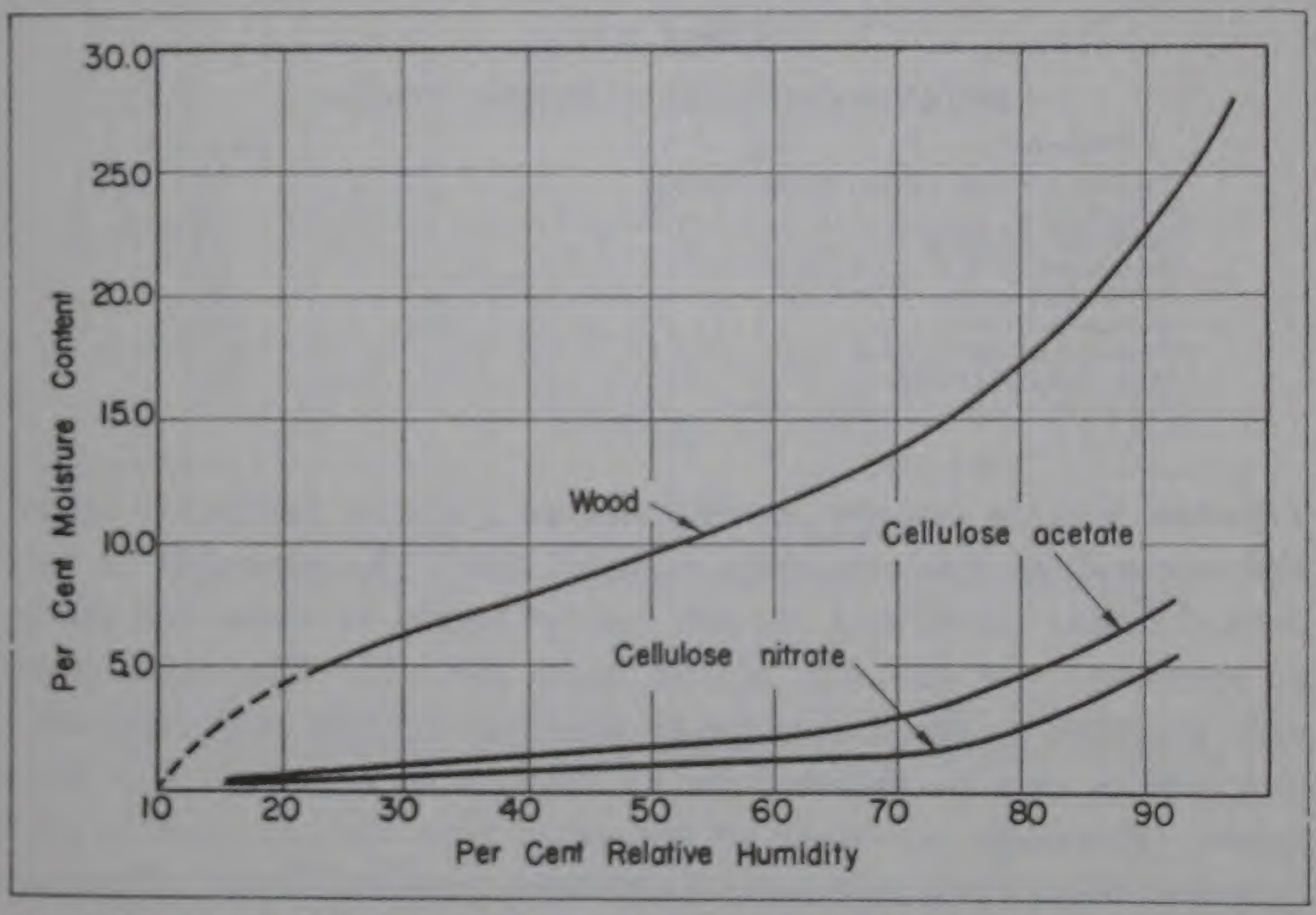


Fig. 52—Results of eight-day test show moisture absorption (vertical ordinate) of plastics when subjected to various relative humidities

Test Methods for Water Absorption and Water Permeation: The relative rate of water absorption of the various plastics is determined by the procedure outlined in ASTM D-570 "Water Absorption of Plastics". Molded specimens generally consist of a 2-inch diameter disk, while sheet specimens are 3 inches by 1 inch in area. Specimens generally are dry-conditioned before test at 50 C for 24 hours. Boiled distilled water is preferred for the immersion medium.

ASTM D-697 "Water Vapor Permeability of Plastics Sheets"

suggests an open-mouth dish which can be sealed by a film of the test specimen. Wax is employed at the edges to insure no loss at this region. A dessicant with a powerful affinity for water (such as anhydrous calcium chloride) is placed in the dish. After sealing, the assembly is exposed to different humidities—such as 50 per cent relative humidity—and the water vapor transmission observed by increase of weight of the dish.

Another method for evaluating the effect of water upon plastics was developed by the author, and based upon changes in dimensions of the test specimen. A short length of material, about

TABLE XLII

Diffusion Constants of Typical Plastics

Material	D x 10^{-8}
Unfilled molded phenol formaldehyde	0.1
Polyethylene	0.2
Polyvinyl chloride	0.5
Polystyrene	3.5
Polymethyl methacrylate	4.1
Polyamide (6-6)	11.2
Cellulose acetate, sheet	36.1
Ethyl cellulose, sheet	78.3
Polyvinyl chloride-acetate, sheet	1.2

5 inches long, is clamped at one end as a simple cantilever beam and covered on one side with a metal foil. The assembly is immersed under water and the side not protected by metal foil picks up moisture and the end of the beam deflects. The method is very sensitive to small changes in moisture content, and comparative results can be obtained on all plastics in a matter of a few hours. Readings are made at the same time the specimen is undergoing immersion, without withdrawing from the liquid. Typical deflection curves, which indicate the extent of dimensional changes because of water absorption, are shown in *Fig.* 53*.

Sunlight and Weather Exposure

The most obvious effects of sunlight upon some plastics is either a slight yellowing of transparent stocks or change in shade of color on colored varieties. Less obvious result for some materials such as natural rubber or cellulose nitrate is a molecular degradation and loss in physical strength. These effects are due in part to the catalytic activity of sunlight upon traces of im-

*J. Delmonte and L. Asselin—*Mod. Plastics*—21, 138, May, 1944.

purities. Among the transparent plastics, polymethyl methacrylate appears to be the least affected of all, though among the newer types coming along, silicone resins appear to age very satisfactorily. Transparent enclosures for aircraft have long standardized upon the acrylics, though improved grades of cellulose acetate permitted some of the latter to be employed. Ethylcellulose

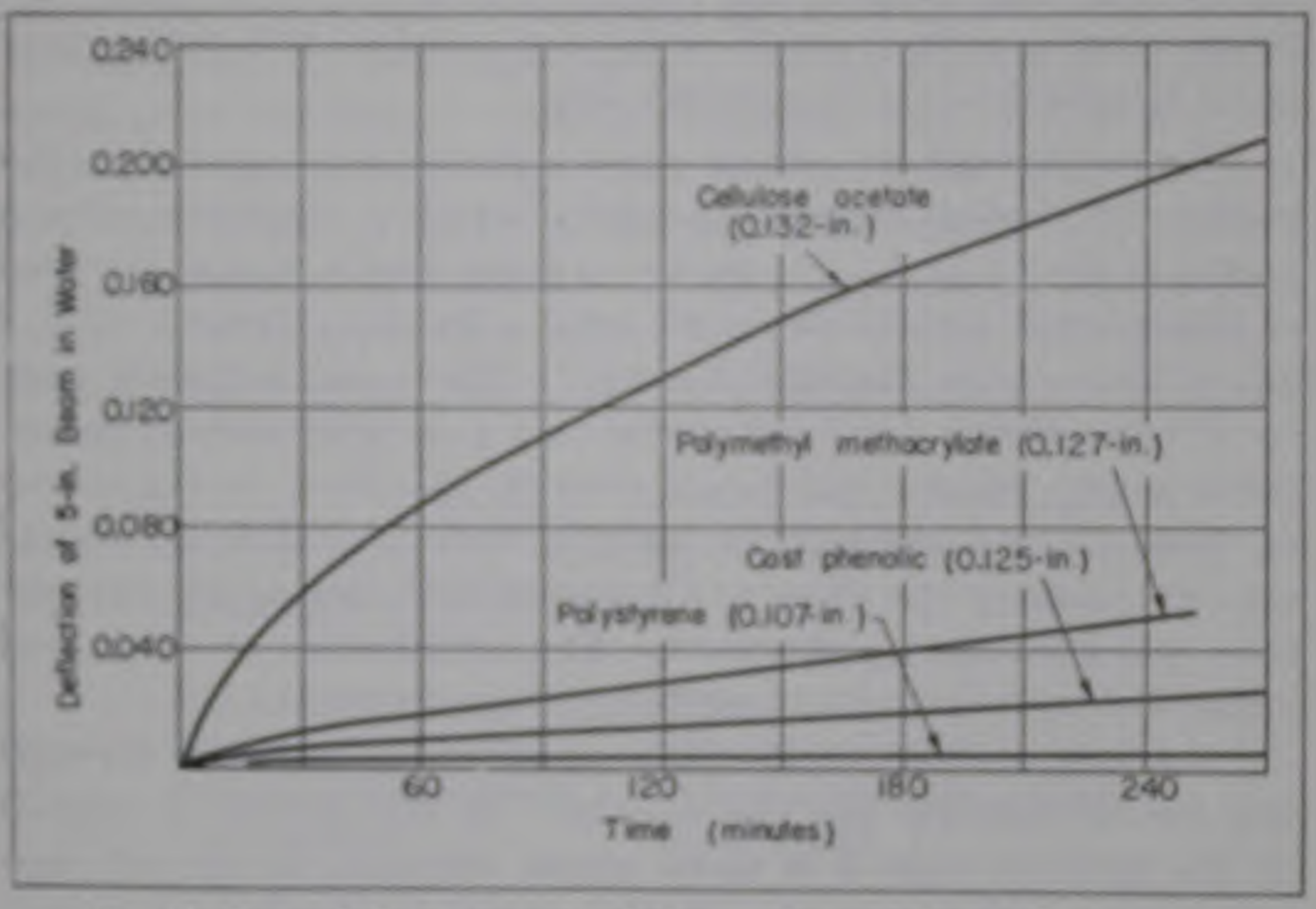


Fig. 53—Curves indicate dimensional changes incurred by water absorption

and cellulose nitrate age quite poorly in sunlight. Polystyrene resins and polyvinyl resins are affected to a lesser extent, though their tendency to discolor in sunlight depends upon the amount of impurities present. Sheets of plate glass, used in safety glass construction, permit longer life of the plastic interlayer in outdoor exposure by filtering out the actinic wavelengths.

Accelerated life tests upon plastics are conducted by exposing the materials to ultraviolet light at slightly elevated temperatures, which promotes rapid deterioration in some circumstances. The ultraviolet light, obtained from direct sunlight or diffused sunlight, is simulated in the laboratory by arc lamps in a weatherometer, or special sunlamps. Cellulosic, acrylic, and urea plastics generally are light stable during exposure to sunlight.

Alternate periods of high humidity followed by low humidity are employed in accelerated life tests upon molded urea parts. Only exceptionally good pieces will withstand several cycles of these conditions. Failures occur in the form of minute cracks near regions where the material has fluxed together improperly or where cracks already have started due to buffing heavy flash.

Corrosion effects such as appear upon the more common metals are absent upon the average plastics. While some materials may absorb a small amount of oxygen, this action may prove beneficial rather than detrimental.

Craze Formation: Small minute cracks may appear on the surface of plastics exposed to outside weather conditions after a period of time. These are known as craze marks, and in the case of transparent plastics are considered a handicap toward obtaining perfect vision through the sheet. For some materials such as cellulose nitrate, the craze marks may grow progressively worse, develop into fissures and break through the sheet in the course of time. Often these craze marks may be duplicated in the laboratory by exposing the sheet to ultraviolet light, drying out the surface, and then flexing the sheet. The combination of stress and ultraviolet light or sunlight will bring about crazing.

Another method of bringing about craze marks is through the use of solvents for the plastics. If the solvent is applied to the material while it is under stress, the craze marks will rapidly develop. For example, wiping benzene or gasoline on curved acrylic pieces will bring about this effect. This method can in fact, be employed for stress analysis in a rather unusual manner. After preparing a transparent plastic model of the indeterminate structure to be tested, apply the stress in the prescribed manner, and while under stress liberally wipe a solvent on the surface. The frequency and the concentration of these craze marks will be a direct measure of the stress distribution. This method has advantages over the brittle-lacquer coatings applied to stressed metal parts, a similar technique which is being increasingly used for estimating stresses.

Effects of Acids and Alkalies

The effects of acids and alkalies upon organic plastics depend upon several variables, including:

1. Strength or concentration of the acid or alkali
2. Temperature of the solution
3. Time the plastics are in contact with solution, and
4. Previous conditioning of plastics.

Increased temperature will definitely accelerate the effect of the acid and alkali. While some materials may withstand attack indefinitely at 40 F, they will be readily attacked at 120 F.

When the plastic is attacked by the acid or alkali the effect generally is one of disintegration rather than dissolving which takes place for metal. This disintegration may be due to an attack upon the molecular structure or some fillers which are present. As a group, however, most plastics exhibit considerably better resistance to acids and alkalies than metals. If the plastic is in a perfectly dry state before it makes contact with a strong acid, it stands better chance of withstanding the effects of the acid.

The halogenated polymers in particular, show marked resistance to strong acids and alkalies. Among those possessing superior resistance are the following:

Chlorinated rubber
Tetrafluoroethylene
Polyvinylidene chloride
Polyethylene
Polyisobutylene
Polydichlorostyrene
Polyvinyl chloride
Polyvinyl chloride-acetate
Polystyrene

These materials in particular are outstanding in their resistance to strong acids and alkalies. However, strong oxidizing acids such as fuming nitric acid will attack most of them, though less severe acid concentrations will be withstood. Polytetrafluoroethylene offers the highest resistance, withstanding boiling aqua regia. In tests upon other more common plastics, the author reported upon the effects of various concentrations of hydrochloric acid, nitric acid, sulphuric acid, and sodium hydroxide upon laminated phenolic, cellulose acetate, cellulose nitrate, and polymethyl methacrylate.* The effect of the acid or alkali was checked periodically by measuring the loss in the strength of the plastic. This proves to be a much more accurate method than measuring weight changes, and permits a quantitative analysis to be made on the

*J. Delmonte—*ASTM Bulletin*—119, 11, Dec., 1942.

performance of the acid or alkali. Typical results are brought out in the accompanying *Figs.* 54 and 55, for laminated phenolics and polymethyl methacrylate.

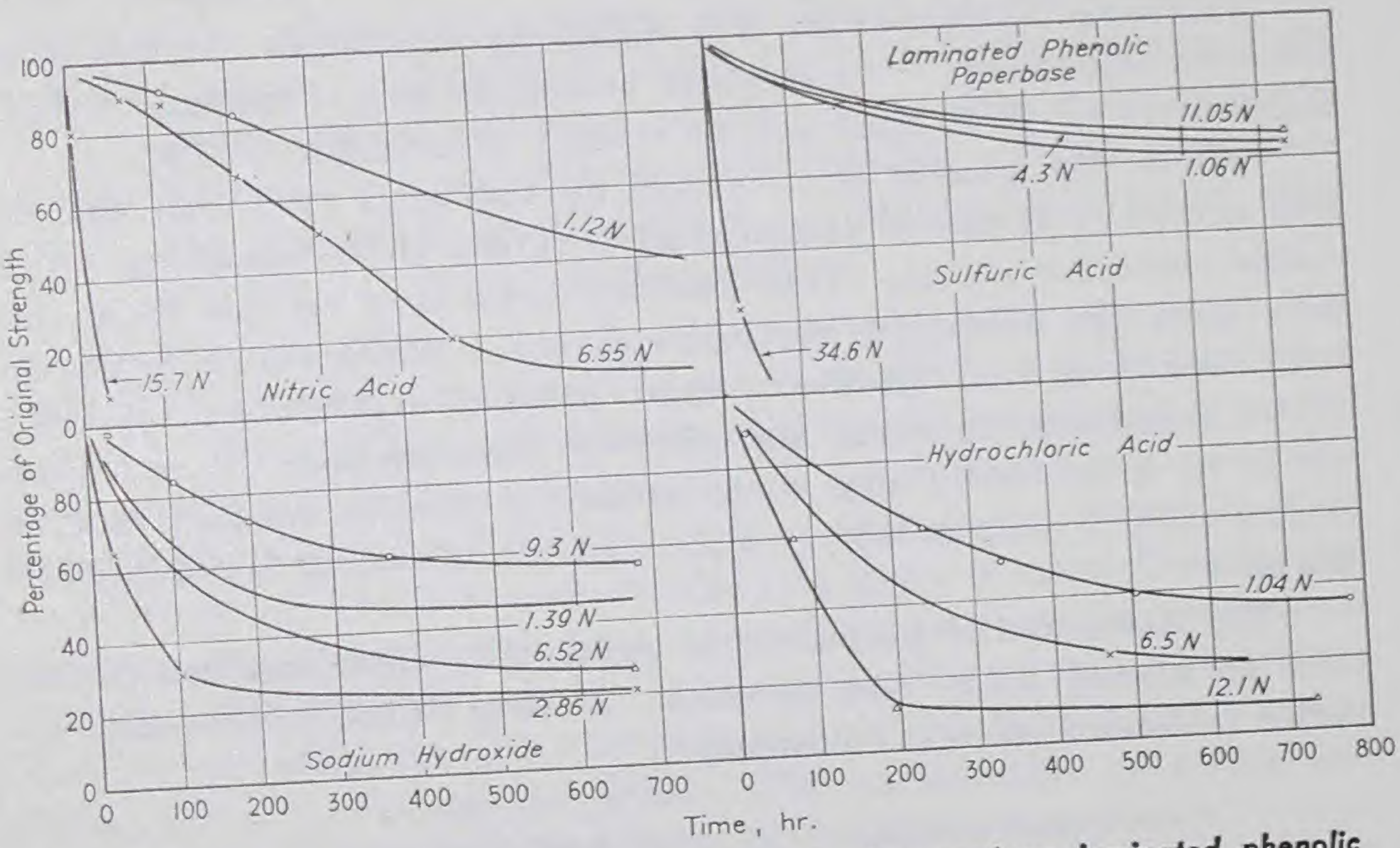


Fig. 54—Effects of various acids on the strength of paper-base laminated phenolic

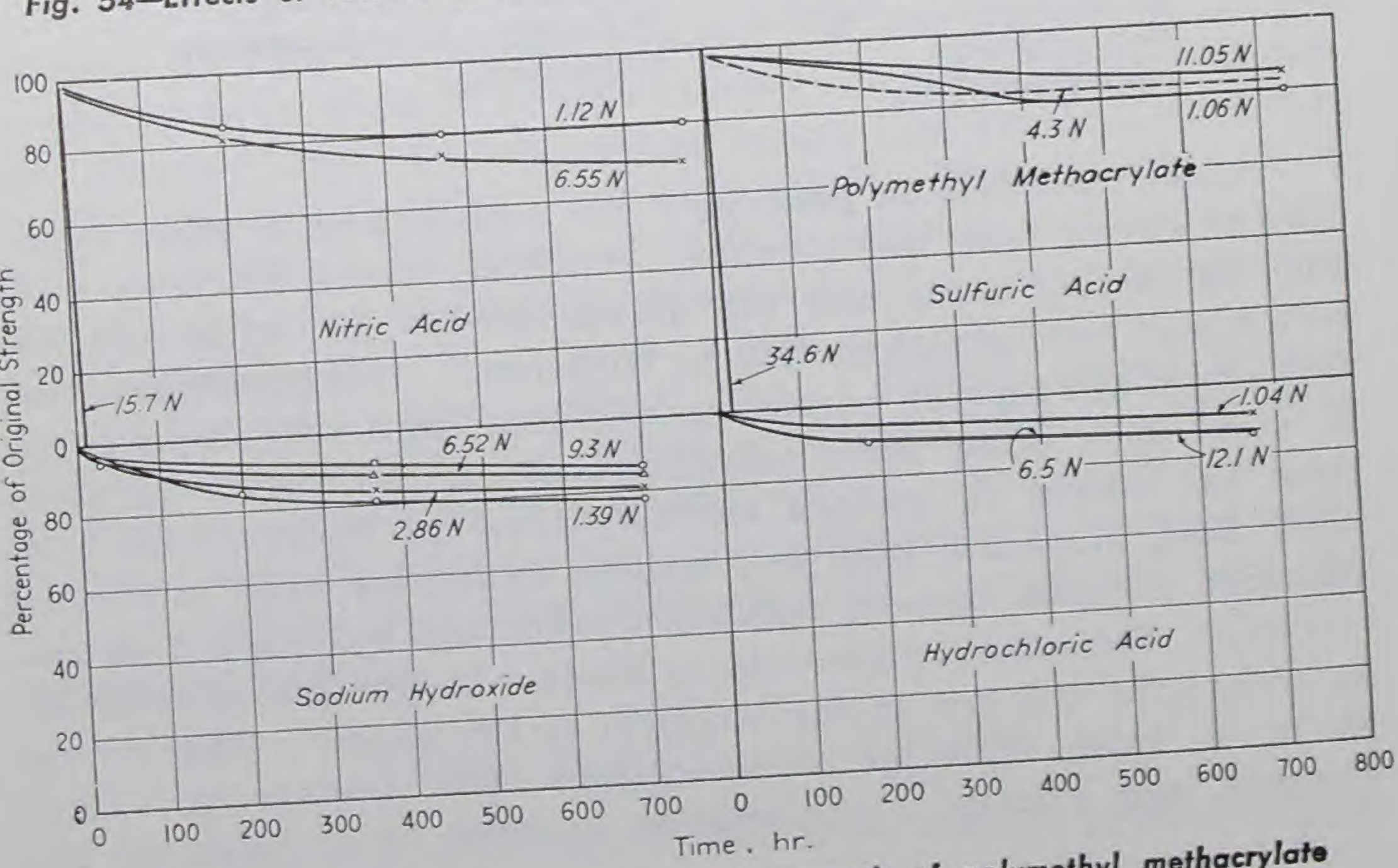


Fig. 55—Effects of various acids on the strength of polymethyl methacrylate

A rather interesting observation is that very strong and very weak solutions of caustic soda do not affect plastics strongly. However, for about 5 normal solution (200 grams per liter of water) of sodium hydroxide, the effect of the alkali is felt most severely.

Tests for Chemical Resistance: ASTM D-543 "Chemical Reagents—Resistance of Plastics To," outlines qualitative procedures for measuring the effects of various chemical reagents, including acids and alkalies, through measurements of weight changes upon the materials immersed for stated intervals.

Effect of Solvents

Knowledge of the effectiveness of solvents is of basic importance to the formulation of cements and surface coatings formulated from plastic materials. In TABLE XLIII representative plastics are compared with respect to their solvent resistance. Those solvents which attack the material most readily are denoted by number 1, and those least satisfactory by number 14. Fourteen representative solvents were chosen for these tests. All samples employed were approximately 0.06 to 0.07-inch thick, and were conditioned dry for 48 hours at 50 C.

In the table, the superiority of cellulose nitrate over other cellulose plastics is clearly recognized with respect to its compatability with various solvents. Acetone is particularly rapid in its effect upon all of the plastics. The effects which the solvents have upon the plastics is designated in the legend below the table. Smooth, good solutions are formed by those solvents which are marked A. In many cases, the solvents cause substantial swelling, while in others the plastics become rubber-like. When solutions are not formed, effect is marked in the table.

Of course this table cites single solvents only. Not to be overlooked are the countless number of binary and tertiary solvent combinations which are effective upon various plastics. For example, ethylene dichloride and methanol are not very rapid in their effect upon cellulose acetate by themselves but they make a good solvent in combination.

The author has found that careful measurements of the loss in strength of a plastic after different periods of immersion in a solvent are the best criteria for tracing the effect of that solvent.

Some organic solvents will lessen the strength down to a certain point and then beyond that not affect the plastic any further. These have been classified as partial solvents, while a true solvent will effect a 100 per cent loss of strength and a true solution. The effects of various solvents, partial solvents, and non-solvents are shown in the accompanying *Figs.* 56 and 57, taken from a recent paper*. These results offer complete quantitative results upon the relative speeds with which plastics are attacked by the different solvents.

TABLE XLIII

Effect of Solvents Upon Plastics

	Material					
Solvent	Polymethyl Methacrylate	Polystyrene	Polyvinyl Chloride Acetate	Cellulose Acetate Butyrate	Cellulose Acetate	Cellulose Nitrate
Ethanol	11*D*	14*E*	14*E*	12*D*	7*D*	7*A*
Methanol	12*D*	14*E*	14*E*	10*D*	6*D*	8*D*
Butyl Acetate	8*A*	8*A*	6*B*	6*A*	9*D*	4*A*
Amyl Acetate	9*A*	9*A*	7*B*	7*A*	10*D*	5*A*
Ethyl Acetate	4*A*	5*A*	5*B*	4*A*	4*A*	3*A*
Butyl Alcohol	14*E*	14*E*	14*E*	13*D*	13*D*	9*D*
Acetone	3*A*	1*A*	1*A*	1*A*	1*A*	1*A*
Methyl Ethyl Ketone	5*A*	3*A*	2*A*	3*A*	3*A*	2*A*
Toluene	6*A*	4*A*	8*D*	11*C*	12*D*	13*D*
Benzene	7*A*	7*A*	9*D*	9*C*	11*D*	12*D*
Carbon Tetrachloride	13*D*	10*A*	14*E*	14*D*	14*D*	14*E*
Ethylene Dichloride	2*A*	6*A*	4*A*	5*A*	5*A*	10*D*
Cellosolve	10*A*	14*E*	10*D*	8*A*	8*D*	6*A*
Chloroform	1*A*	2*A*	3*B*	2*A*	2*A*	11*B*

Key to Symbols:
1, Most rapid in effect; 2, the next rapid; consecutively to 14, the least rapid
A Complete dissolving of plastic which enters solution
B Complete disintegration of plastic with loss of all shear strength
C Substantial swelling accompanied by loss of shear strength to a constant value
D Loss of shear strength to a constant value—no dissolution
E No effect at all.

The thermosetting plastics may be attacked by solvents if they are not fully cured or if they contain some extractable matter. By grinding up a given specimen to a fine powder, and extracting with acetone upon a reflux for several hours, the state of cure of the material can be determined (ASTM D-494 "Acetone Extraction Test of Phenolic Molded or Laminated Specimens"). It is also possible, in the case of undercured materials, to measure a loss in strength after immersion or refluxing with acetone.

While the above figures indicate the effects of a number of typical solvents upon plastics, it may be desirable to supplement this information with additional notes upon true solvents or sol-

*J. Delmonte—*Ind. & Eng. Chem.*—34, 764, June, 1942.

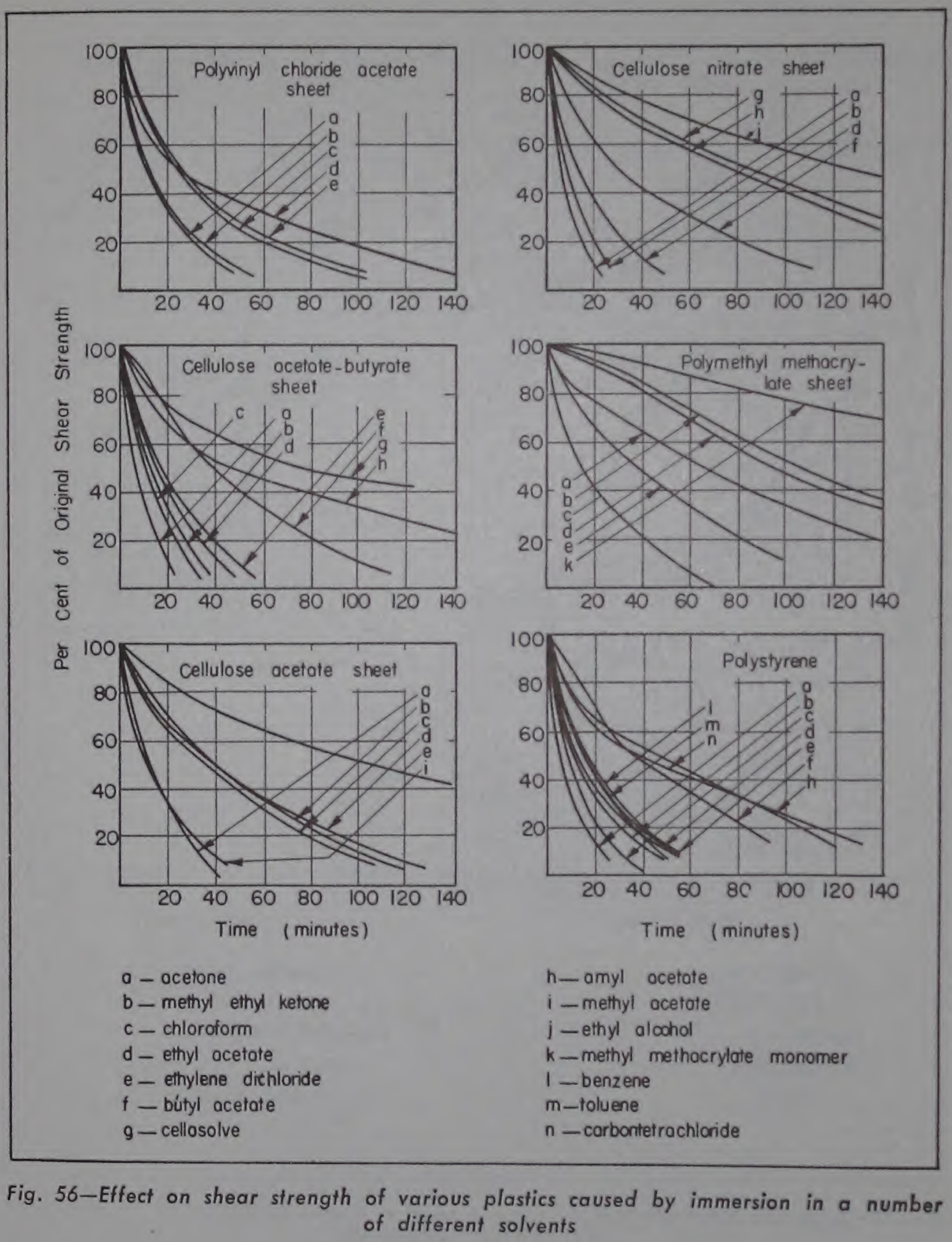


Fig. 56—Effect on shear strength of various plastics caused by immersion in a number of different solvents

vent combinations for representative plastics. These are presented in the following paragraphs in itemized form:

POLYMETHYL METHACRYLATE: While chloroform acts the fastest, also effective are glacial acetic acid, ethylene and methylene dichloride, furfural, acrylic monomer, and vinyl acetate.

POLYSTYRENE: Acetone, benzene, toluene, and carbon tetra-

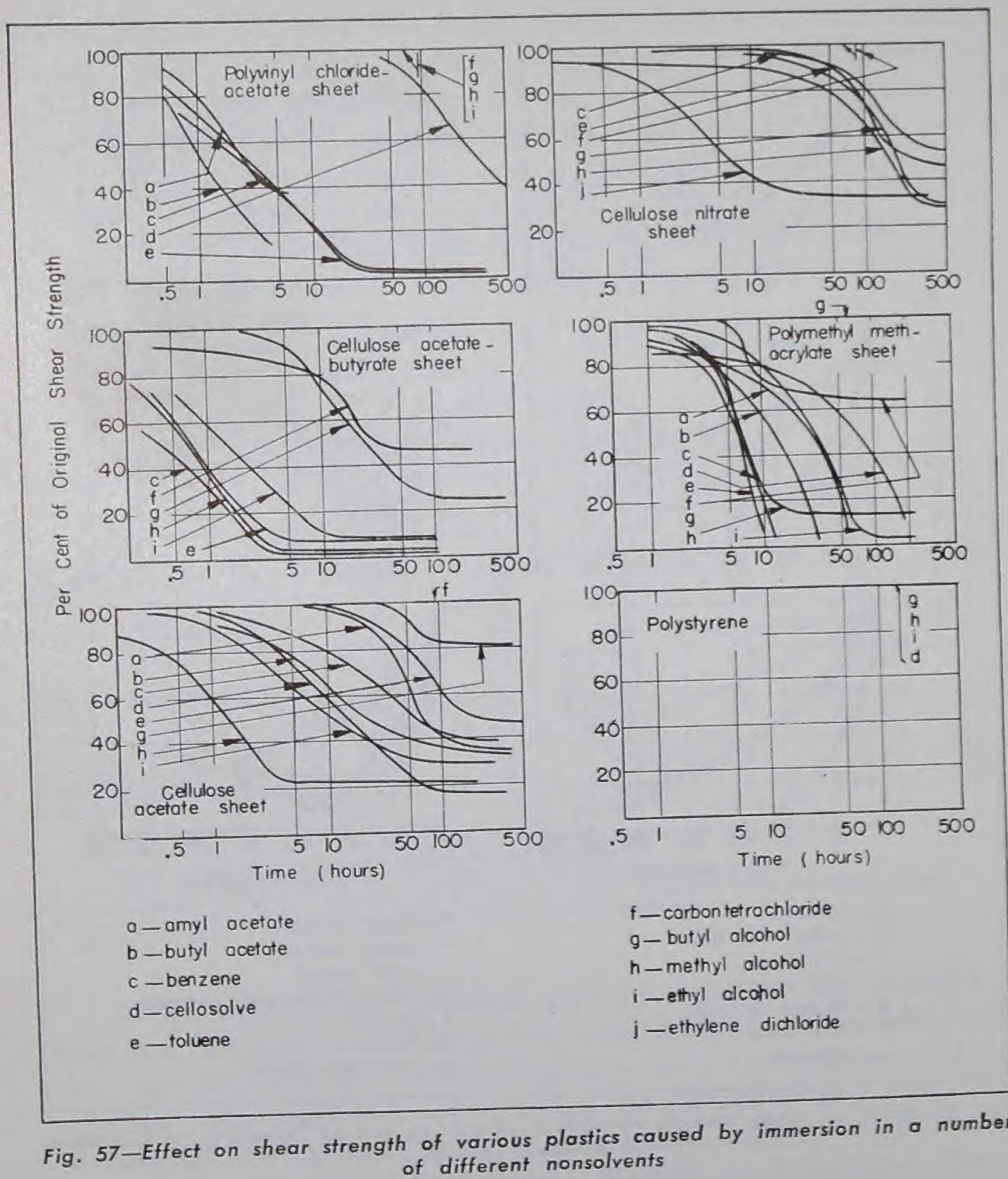


Fig. 57—Effect on shear strength of various plastics caused by immersion in a number of different nonsolvents

chloride are good.

ETHYL CELLULOSE: Acetone or combinations of 80 per cent benzene with 20 per cent alcohol.

POLYVINYL CHLORIDE-ACETATE (high in chloride): Cyclohexanone, acetonyl acetone, isophorone, methyl isobutyl ketone, or mesityl oxide will dissolve the material effectively.

POLYVINYLIDENE CHLORIDE: Quite resistant to all solvents.

Hot orthodichlorobenzene will form a 2 per cent solution.

POLYETHYLENE: Resistant when cold. Hot aromatics such as benzene will dissolve.

POLYVINYL BUTYRAL: Various alcohols and furfural good solvents.

POLYAMIDES: Resistant to solvents. Hot formic acid, molten phenol, or molten resorcinol will dissolve.

CELLULOSE DERIVATIVES: Acetone, ethyl acetate, amyl acetate, etc., are typical.

Chapter VIII

Optical Properties of Transparent Plastics

The large majority of commercial organic plastics are available in transparent forms, and for these a number of important engineering applications have been developed. Interest in transparent organic plastics arises not so much from their optical properties as their favorable mechanical characteristics. In the transparent plastic material, the engineer finds a material which readily can be machined into a number of complicated shapes, or if quantities are involved, molded with a high degree of accuracy. Unlike the fragile, easily broken inorganic glasses, transparent plastics are substantial materials possessing a good degree of toughness.

The greatest single drawback of transparent plastics is their lack of scratch resistance, the majority of the materials being readily abraded by dust and sand. While some grades of polyesters have demonstrated a marked improvement in abrasion resistance, this has been accomplished at a sacrifice in toughness and impact strength. Other experimental efforts have achieved an improvement in surface hardness, leaving a tough core, through certain types of heat treatment or through the use of special processing chemicals.

Among the best known applications of transparent plastics are enclosures for bomber noses or canopies for fighter aircraft. *Fig.* 58 shows a typical unit of this description. Tough, optically clear, these enclosures have one-half the weight of glass. During the Second World War, practically the entire production of polymethyl methacrylate went into the manufacture of transparent sheets which were formed into aircraft enclosures. Much activity was evidenced in the development of special forming and drawing techniques to produce optically clear structures. These transparent plastics served more than as a viewing window, because important components of machine guns as well as sighting mechanisms have been mounted upon and fastened directly to them.

Index of Refraction

Indices of refraction of various plastics are shown in TABLE XLIV. High upon the list is polyvinylidene chloride. The refractive index is a ratio of the sine of the angle of incidence to the sine of the angle of refraction, and in terms of light bending

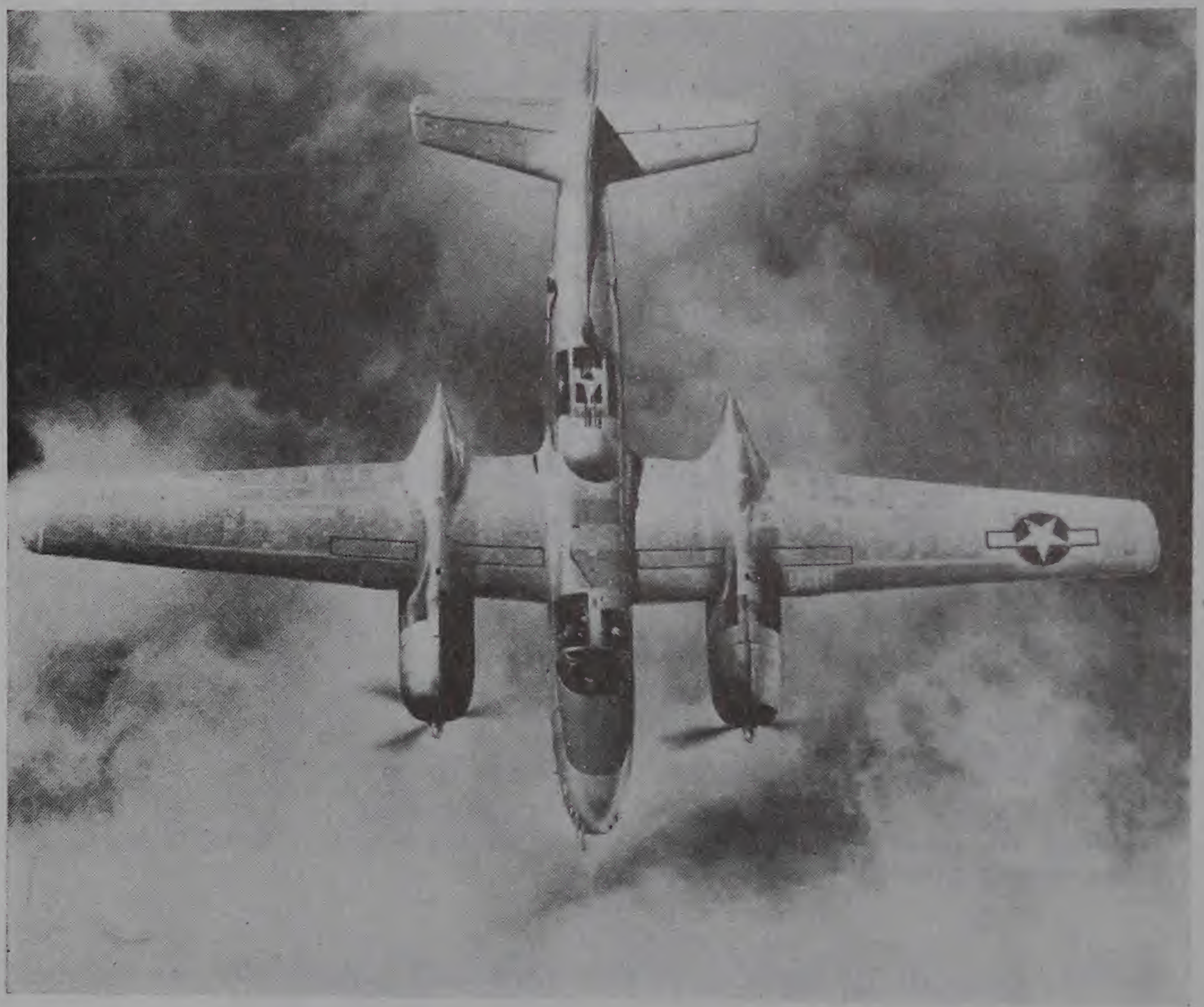


Fig. 58—Pilot canopy of this attack bomber is transparent methyl methacrylate; one-half the weight of glass

phenomena within a transparent body, this means that a higher proportion of light can be transmitted through the length of the transparent medium.

The maximum possible light transmission for any material having two flat and parallel surfaces is given approximately by the following equation:

$$\text{Per cent transmission} = \left(1 - \frac{(n-1)^2}{n^2+1}\right) \times 100$$

where n is the index of refraction.

Thus, for example, the maximum theoretical transmission for a flat sheet of acrylic is 92.4 per cent, the balance being lost as reflected light, even though the light be perfectly normal to the surface. Corrected for this reflected light, however, the transmission would be 100 per cent. There are developments, however, in which materials with a low index of refraction are applied to glass surfaces as a surface film, a treatment which improves light transmission*.

TABLE XLIV

Optical Properties of Plastics

Transparent Material	Index of* Refraction	Critical Angle of Internal Reflection	Max. Theoretical Light Transmission (%)
Phenol formaldehyde, cast	1.59–1.62	38° 24′	89.3
Urea formaldehyde, translucent	1.54	.....	...
Melamine formaldehyde, translucent	1.60	.....	...
Polymethyl methacrylate	1.488	42° 15′	92.4
Polystyrene	1.59–1.60	38° 50′	90.0
Cellulose acetate, sheet	1.48–1.50	42° 15′	92.4
Cellulose nitrate, sheet	1.49–1.51	41° 45′	92.3
Allyl, Type (CR-39)	1.50	41° 45′	92.3
Polyvinyl chloride-acetate	1.52–1.53	40° 55′	91.7
Ethyl cellulose	1.47	42° 50′	93.0
Polyvinylidene chloride	1.60–1.63	38° 15′	89.5
Polyamide	1.53	40° 45′	91.5
Polyethylene	1.52	41° 10′	91.8
Ordinary crown glass	1.5174	41° 15′	91.8
Ordinary flint glass	1.613	38° 15′	89.6
Very heavy flint glass	1.778	34° 12′	85.6
Diamond	2.42	24° 24′	70.5

* These indices of refraction are determined for the D lines of sodium (wavelengths 5896 and 5890 Angstroms—1 Angstrom $=10^{-8}$ cm.)

The amount of light lost per surface by reflection is one-half that from a flat sheet with two surfaces. In the accompanying *Fig.* 59, the percentage of light reflected at the first surface of acrylic is shown for different angles of incidence. Experimental results have been shown to check theoretical values quite closely. Calculations are according to the following formula:

$$\text{Reflected light} = \frac{1}{2}\left[\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)}\right] I$$

where i = angle of incidence
r = angle of refraction
I = incident light.

*F. Jones—*Jl. Opt. Soc. Amer.*—31, 34, Jan., 1941.

Another significant figure which determines the effectiveness of a transparent plastic as a light bending medium is the critical angle. The critical angle is defined as follows:

$$\text{sine of critical angle} = \frac{1}{\textit{index of refraction}}$$

The larger the index of refraction the smaller the critical angle (measured from the perpendicular to the surface) and the greater will be the proportion of light capable of re-reflection within the transparent material. This is illustrated in the sketch for a transparent material, *Fig.* 60. The minimum recommended radius of bend is approximately three times the thickness of the sheet or diameter of the rod being bent.

The light-bending characteristics of transparent plastics plus their good crystal-clear transparency have made them popular materials in the design of various optical goods. One instrument manufacturer developed a light-diffusion ring whereby, from a single source of light, the light was "piped" around the periphery of an instrument dial face, spreading the light uniformly over all

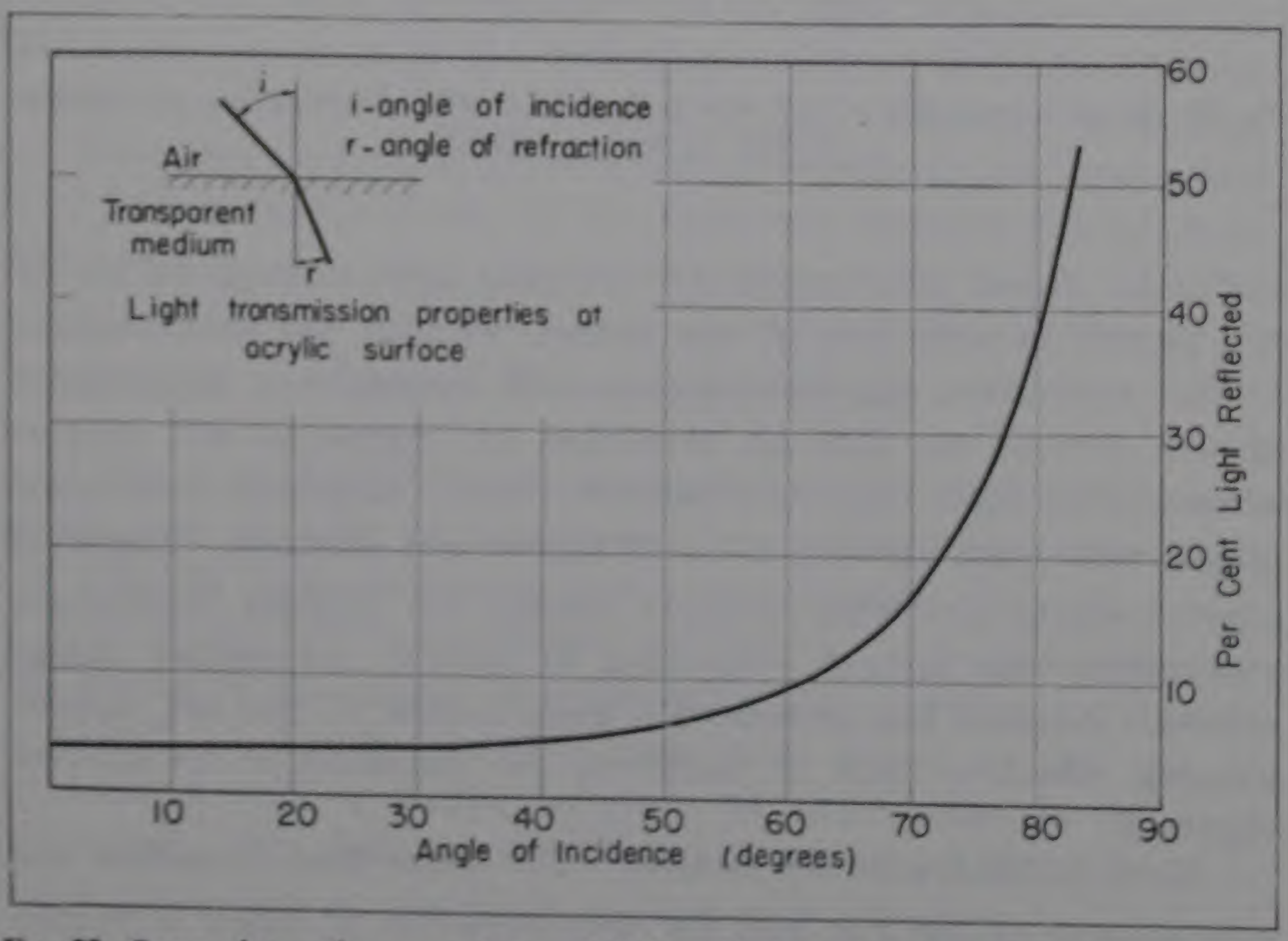


Fig. 59—Curve shows the percentage of light reflected at first surface of acrylic for different angles of incidence

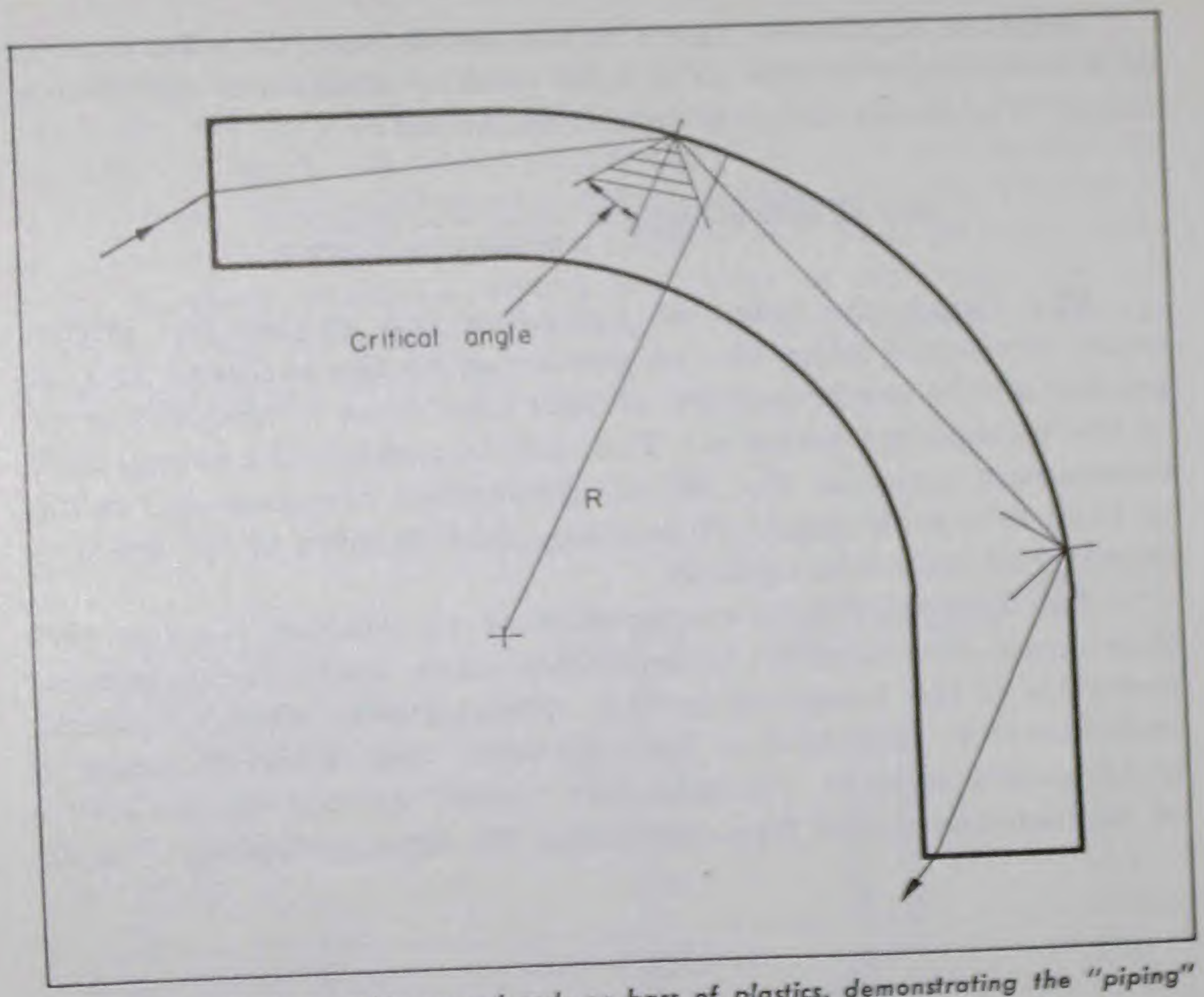


Fig. 60—Re-reflection within curved rods or bars of plastics, demonstrating the "piping" of light through a material

surfaces. Small instruments for carrying light through an acrylic rod permit examination of the throat, without the inconvenience of the heat from the light source. Of course, any interruption of the surface as through scratches or engraving will capture some of the light rays and redirect them. Engraved instrument panels with edge lighting are well known and effective. Engraved acrylic sheets are quite popular among the plastics fabricators, who utilize the optical properties to achieve interesting design effects. Pearson has presented a good review of this art, demonstrating effective ways of designing for brilliance in transparent plastics.*

Test for Index of Refraction: The flame from a sodium salt is preferred as the standard for determination of index of refrac-

*H. F. Pearson—*Plastics*—2, 88, June, 1945.

tion. Measurements are made with the aid of an Abbe' refracometer or with, a microscope equïpped with microscopic measurements of longitudinal travel. ASTM D-542 "Index of Refraction of Transparent Organic Plastics" outlines the technique followed in making measurements.

Dispersion

While the index of refraction is commonly determined for the wavelengths of light corresponding to the D lines of sodium spectrum, this value of the index of refraction differs for other wavelengths of light. The differences, while small, are nevertheless of great significance to the design of precision lenses and optical goods. The differences of indices of refraction for optically visible wavelengths of light are known as dispersion, and the greater the degree of dispersion the greater the amount of chromatic aberration.

General data on the dispersion of all transparent plastics are not generally available, though some good data have been made for polymethyl methacrylate. The dispersion, defined as the difference in the index of refraction for the 4861 Angstrom and the 6563 Angstrom lines of the hydrogen spectrum, is 0.008. Shown graphically, this would be represented approximately as in *Fig.* 61. Compared with some glasses, this dispersion is low, and would be evidenced, for example, by the spectrum dispersion in a triangular prism.

Haze of Transparent Plastics

Using a photoelectric cell the sensitivity of which to different wavelengths of light is comparable to that of the human eye, it is possible to measure the haze in transparent plastics as well as some of the light transmission properties. A small 6-volt light bulb serves as the source of light, being placed within a cylindrical shield. A 1-inch diameter aperture is placed at the end of the cylinder, with a similar aperture 18 inches away in front of a photocell. The light transmission is determined with no specimen in place, and by the light reading on a 100-microammeter instrument connected in series with the photocell. The decrease of photoelectric current, with the transparent specimen in place is

observed on the microammeter. The haze is computed from the difference of the microammeter readings with the specimen nearest the light source, and the specimen when placed adjacent to the photocell, 18 inches away. The entire assembly is enclosed within a blackened box.

Test for Haze: ASTM D-672 "Test for Haze of Transparent Plastics" describes the apparatus for determining light transmission and haze with the aid of a photoelectric cell.

Haze values are greater for the molding compositions than the clear sheets. Another rough empirical method employed in the inspection of curved sheets of transparent plastics is a small telescope focused upon a graph paper a short distance away. The specimen is inserted between the lens and the graph paper, and distortion of the image observed. While this telescopic examina-

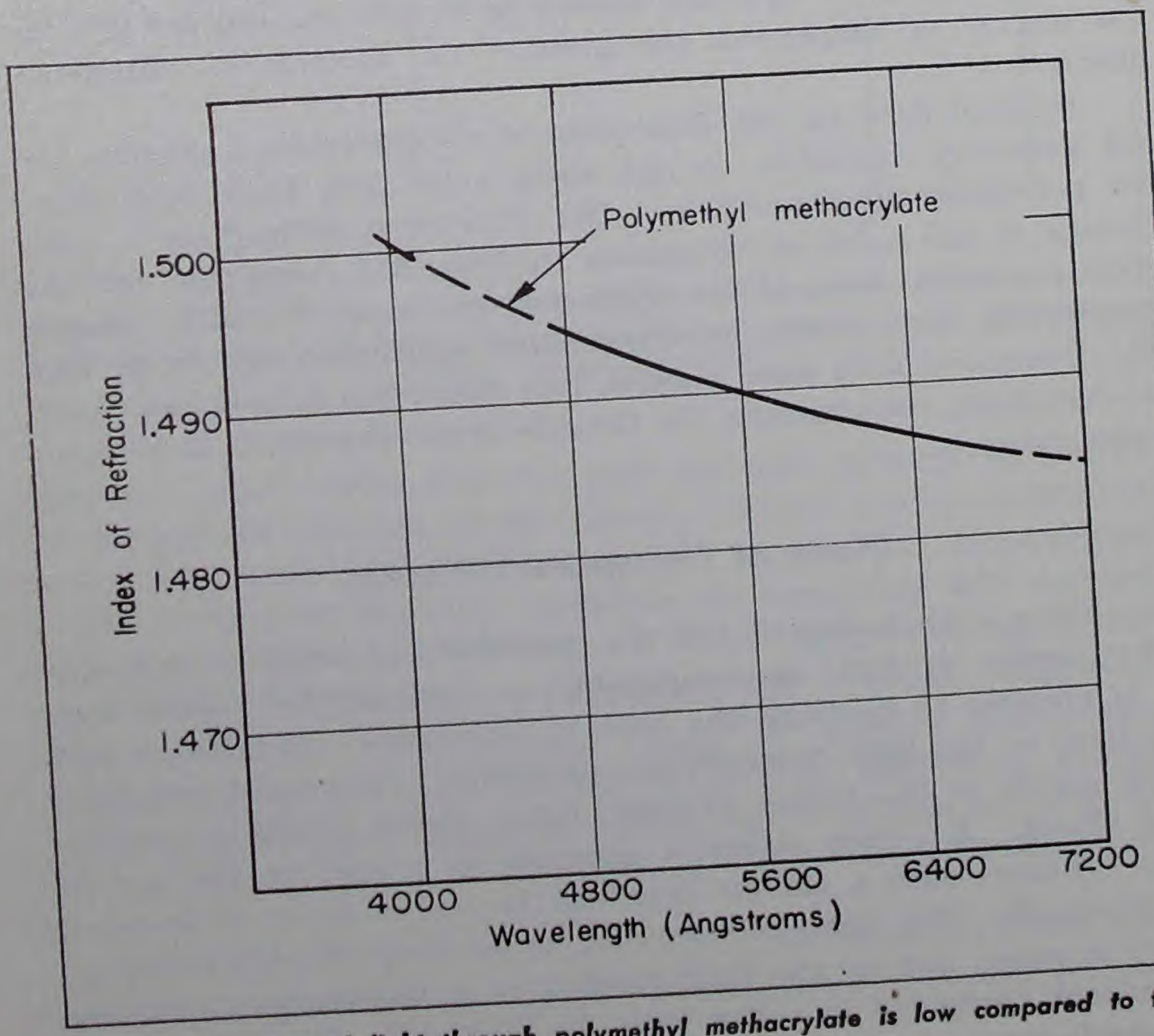


Fig. 61—Dispersion of light through polymethyl methacrylate is low compared to that of many glasses

tion is intended to show up internal strains and optical flaws in formed sheets, it will also reveal the presence of excessive haze.

The ASTM method of measuring light transmission as described above, always has been highly useful in determining the effects of sunlight upon transparent plastics. Light transmission properties are determined through comparison with a control specimen. The others are exposed to outside weather for different intervals of time. Typical results are shown in TABLE XLV.

TABLE XLV

Typical Characteristics of Transparent Plastics

Plastic	Light Transmission—As furnished (per cent)	Light Transmission—After 60 days* (per cent)
Methyl methacrylate	92	91.5
Plate glass	90	90
Cellulose acetate	90	87
Cellulose nitrate	89	83
Urea formaldehyde	89	..
Polyvinyl chloride-acetate	87	78
Glyceryl phthalate	86	82

* Exposure to weather.

Spectral Transmission of Transparent Plastics

The spectral transmission characteristics of transparent plastics have differed from ordinary glass, stimulating new interest and applications in the near, ultraviolet, and infrared. Using specimen sizes of 1¼ by 1⅝ by 0.150-inch, Rice, Fiedler, and Pyle have reported on the light transmission characteristics of a large number of plastics from 2200 to 13000 Angstroms*. These data are the most complete ever published about transparent plastics, and a portion of their results are illustrated in *Fig.* 62. The polymethyl methacrylate resins possess the largest percentage of light transmission in the ultraviolet region. The polyester illustrated in *Fig.* 62 is "Selectron".

Transmission of Ultraviolet Light

In the design of engineering structures a thorough and accurate mathematical analysis of stresses in load carrying members is of utmost importance. Mathematical theories of stress analysis generally compute average rather than exact point-to-point stress distribution. Approximations as the structure be-

*J. Delmonte—*Trans. ASME*—68, 241, April, 1946.

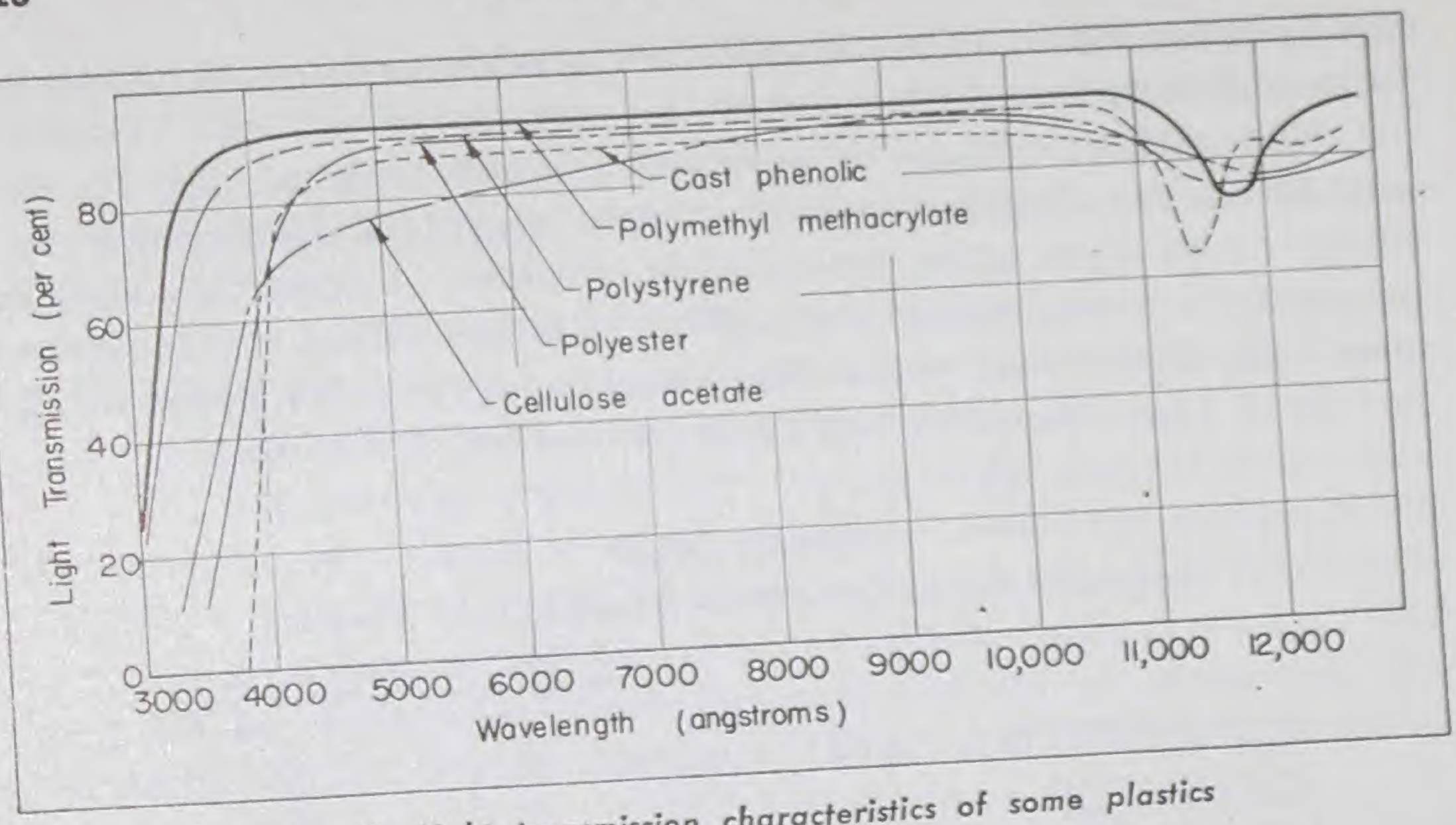


Fig. 62—Light transmission characteristics of some plastics

comes more complicated increase the possibility of misleading calculations. Photoelastic methods allow an experimental analysis of a proposed structural design, avoiding possibility of failure of over-stressed members not observed in the mathematical analysis. Constructive improvements in the design of machines often are realized through this useful method of analysis.

Transparent plastic models employed in the photoelastic method of analyzing stress distribution are stressed in the same manner as the proposed metal members. Through optical methods, the stresses are ascertained qualitatively and quantitatively. An important consideration is the fact that the stress distribution is appreciably the same for plastics and metals, up to the elastic limit.

Application of stress to a transparent plastic model induces temporary double refraction, which is manifested optically when polarized light is passed through the model. As a wave motion, light vibrates in all directions at right angles to the beam direction. When the light is polarized in one plane of vibration, the beam is divided into two systems of transverse waves because of double refraction in the stressed transparent-plastic member. The light passes from the model through an analyzer, which shows the interference effects of the two emerging waves out of phase with each other. When monochromatic light from a mer-

cury arc is employed, the effect is observed in light and dark fringes, originating from the sources of stress concentration. White light gives colors not as well defined as the dark and light fringes.

Optical analysis by photoelastic analysis is less laborious than some mathematical calculations, and more nearly correct for complicated structures. Parts of machines which frequently are studied by this method are fillets, frames, notches, holes, and discontinuities of all types in load-carrying members. Dr. M. Hetenyi has conducted much work in the photoelastic analysis of stressed machine elements. One of his contributions has been an analysis in three dimensions, rather than flat patterns. After the transparent plastic member has been annealed and then frozen in a stressed condition, a thin sample is sliced from the body for photoelastic analysis. In *Fig.* 63 is demonstrated a study of this nature upon various types of nut and thread assemblies. The transparent material was cast phenol-formaldehyde, which shows a high degree of optical sensitivity. The numbers in the diagram indicate the relative degrees of stress concentration.

Plastic materials have contributed immeasurably to studies of this nature. Not only have they made available materials with a high degree of stress-optical sensitivity, but they have also made practical the development of polarizing glasses, upon which this analysis is predicated. Crystals of herapathite, a sulfate of iodo-quinine, are suspended upon a thin plasticized sheet of cellulose ester or poylvinyl ester. Upon stretching the sheet the crystals are oriented. In this manner "Polaroid" has been developed into large sheets, making the polarizing of light accessible to many laboratories and industrial establishments. More recently, orientation of polyvinyl resin sheets alone, have possessed necessary light polarizing characteristics.

Stress-optical sensitivities of various plastics are compared in the accompanying Table XLVI. It will be noted that glass

TABLE XLVI

Optical Constants of Transparent Plastics

Material	Brewsters Coefficient	Optical Sensitivity
Glass	2.7	1.0
Cellulose nitrate	11.1	4.1
Cellulose acetate	19.5	7.2
Phenol formaldehyde	50.0	18.5
Allyl type (CR-39)	86.6	32.0
Cast phenol formaldehyde	132.0	49.0

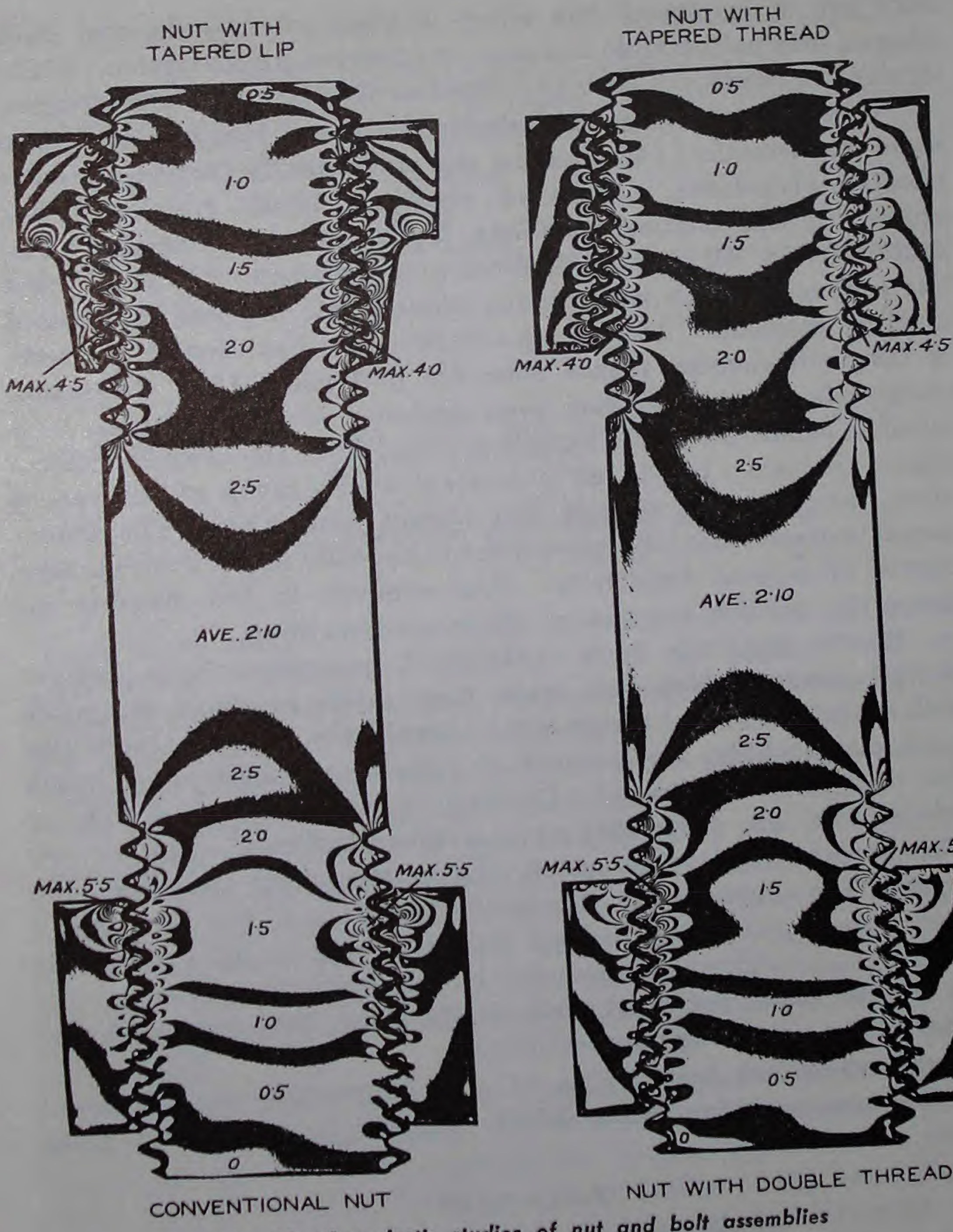
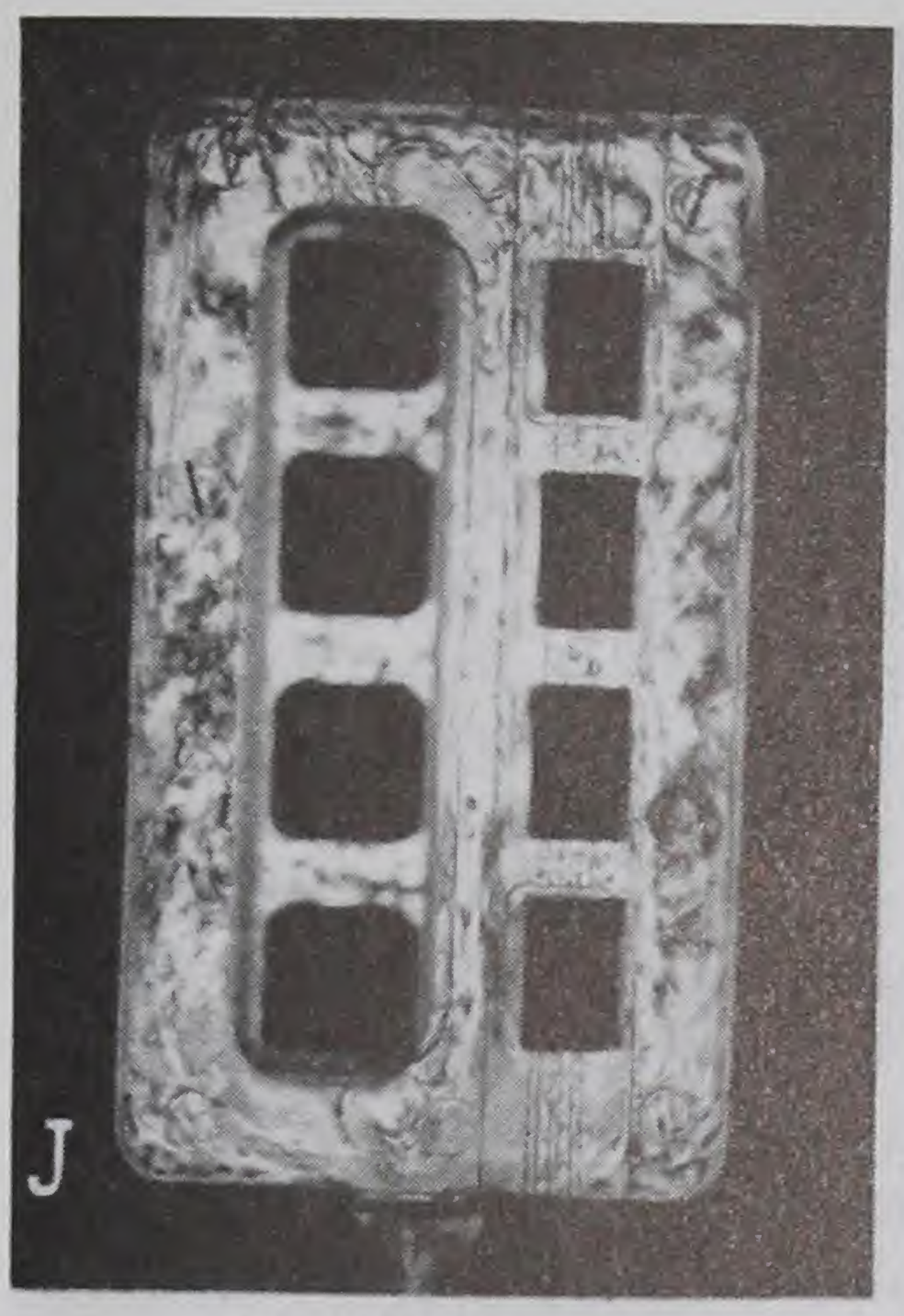
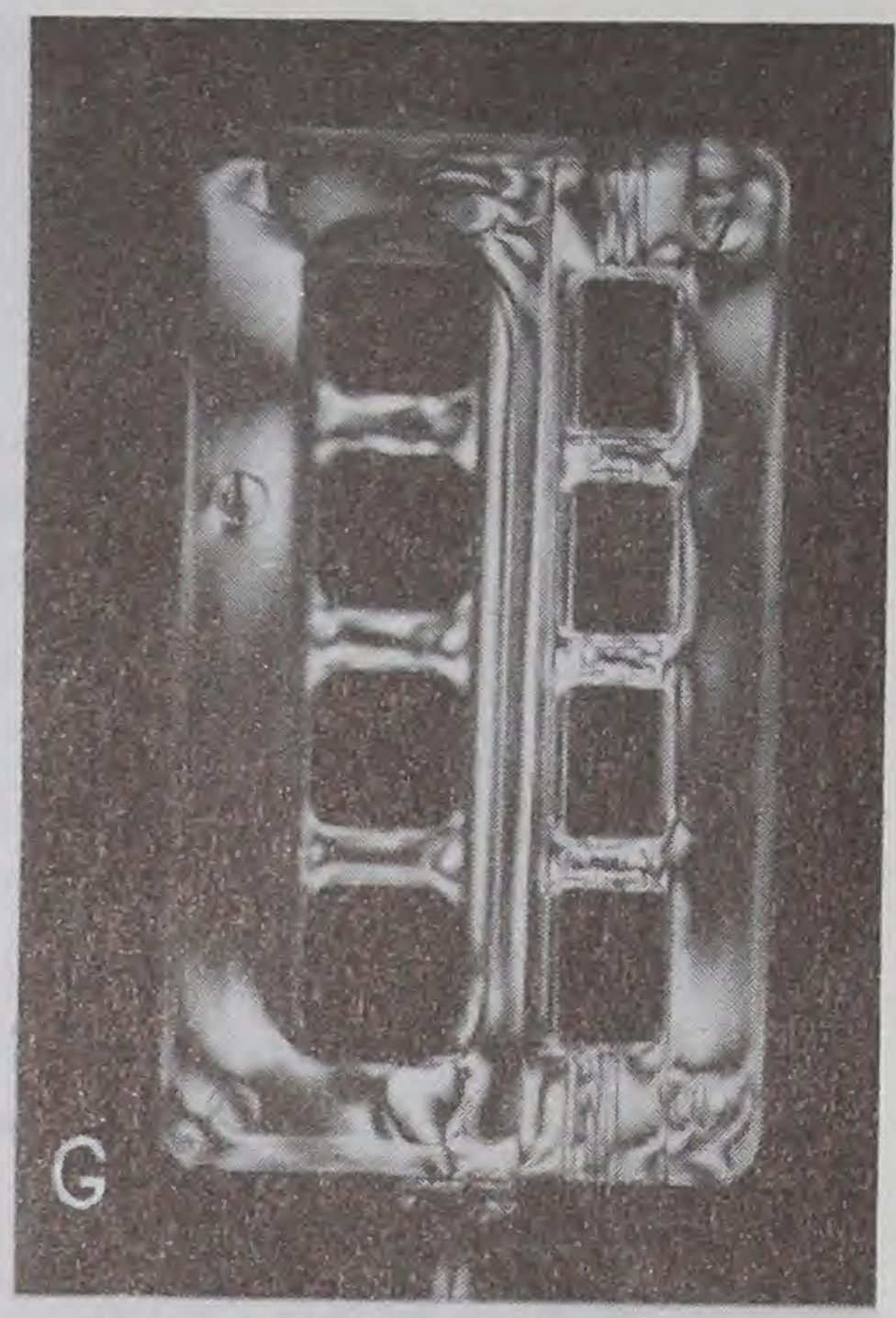


Fig. 63—Photoelastic studies of nut and bolt assemblies

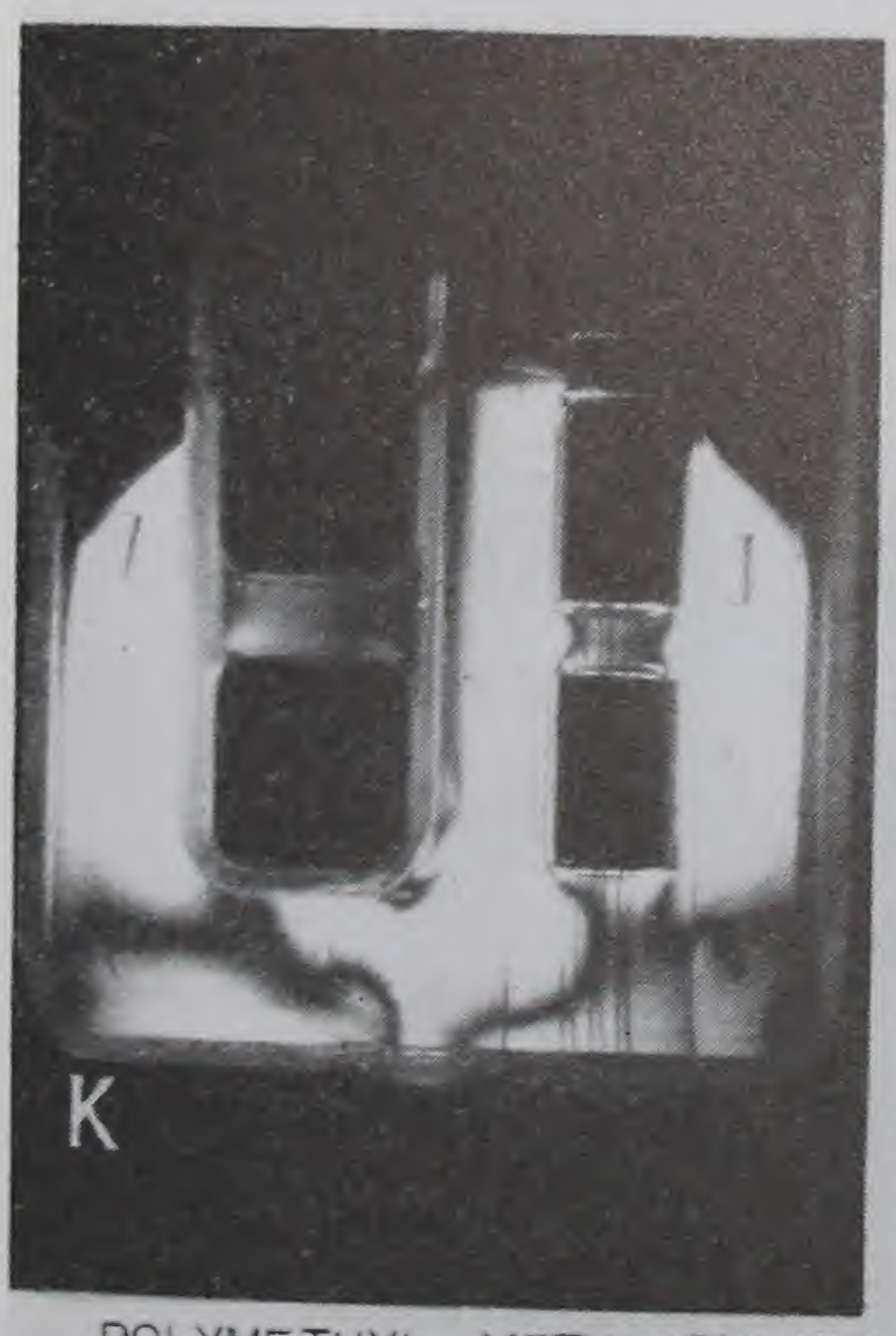
is very poor from the standpoint of stress-optical sensitivity, though cast phenolics and allyl type resins are outstanding. The stress-optical sensitivity is based upon the amount of stress required to cause one light and one dark fringe during examination



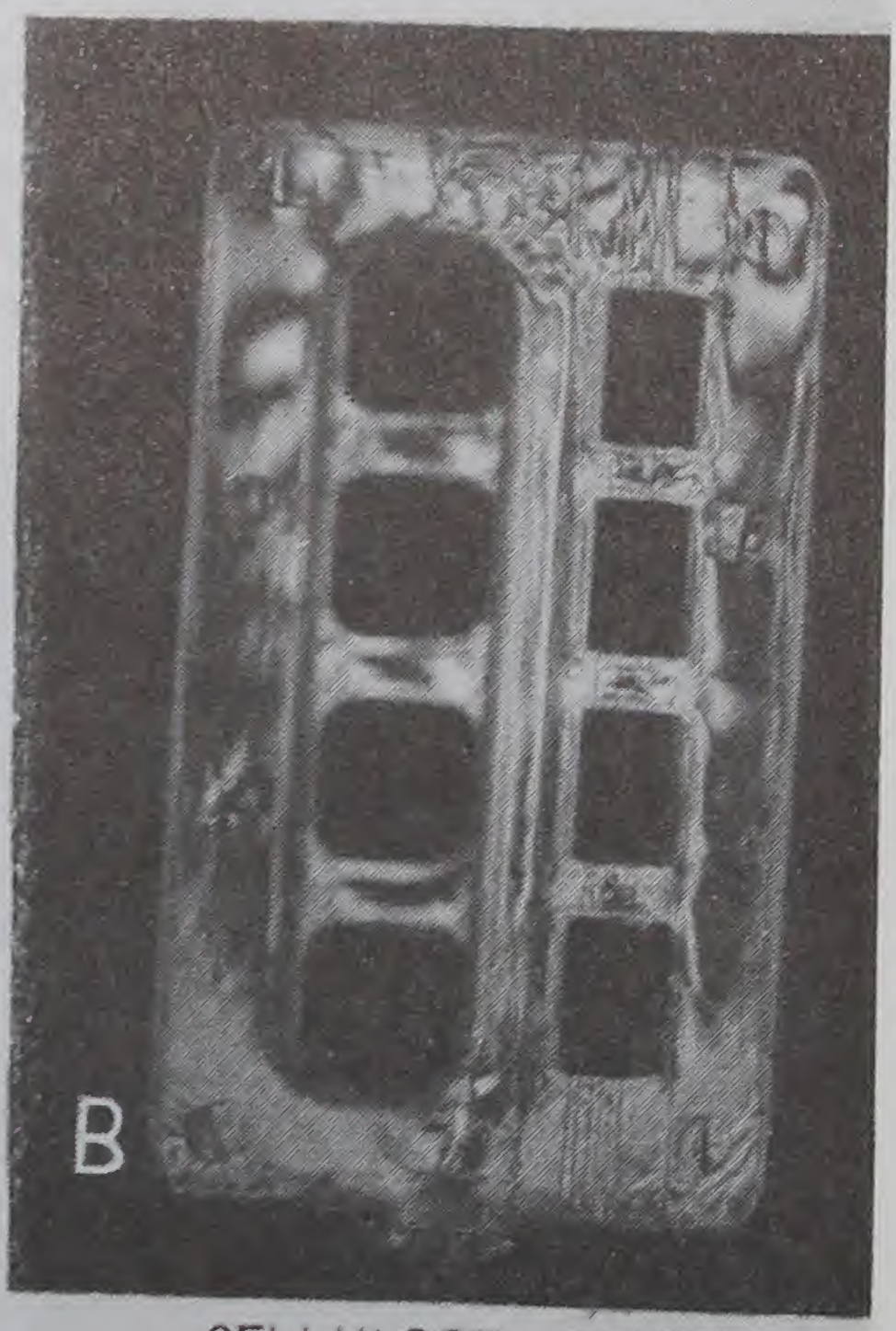
POLYSTRENE



CELLULOSE ACETATE - BUTYRATE



POLYMETHYL METHACRYLATE



CELLULOSE ACETATE

Fig. 64—Photoelastic studies help in determining the effects of molding temperatures, pressures, and injection rates

in polarized light. The greater number of fringes formed during the application of a unit stress, the higher the degree of accuracy with which the examination may be conducted. The absolute unit is the brewster, which equals 10^{-13}dyne/cm^2.

The author has found the adaptation of photoelastic analysis to the study of transparent moldings to be a highly useful technique for determining the effects of different molding pressures, molding temperatures, and different rates of injection (during injection molding). The various plastics each have their own characteristic photoelastic pattern, as demonstrated in *Fig.* 64. Least sensitive of all is the acrylic plastic, which shows only few fringes for the internal strains which are present. More irregular than other materials is the pattern of polystyrene. All of these articles were produced by injection molding under substantially equivalent conditions. Internal strains determined in this manner can be alleviated at times through redesign and relocation of the injection gate.

Photodielectric Analysis of Materials

The author has also found that examination of transparent plastics under high voltage gradients by means of polarized light is a useful tool for studying the effects of voltage gradients in solid dielectrics. The technique has been named photodielectric

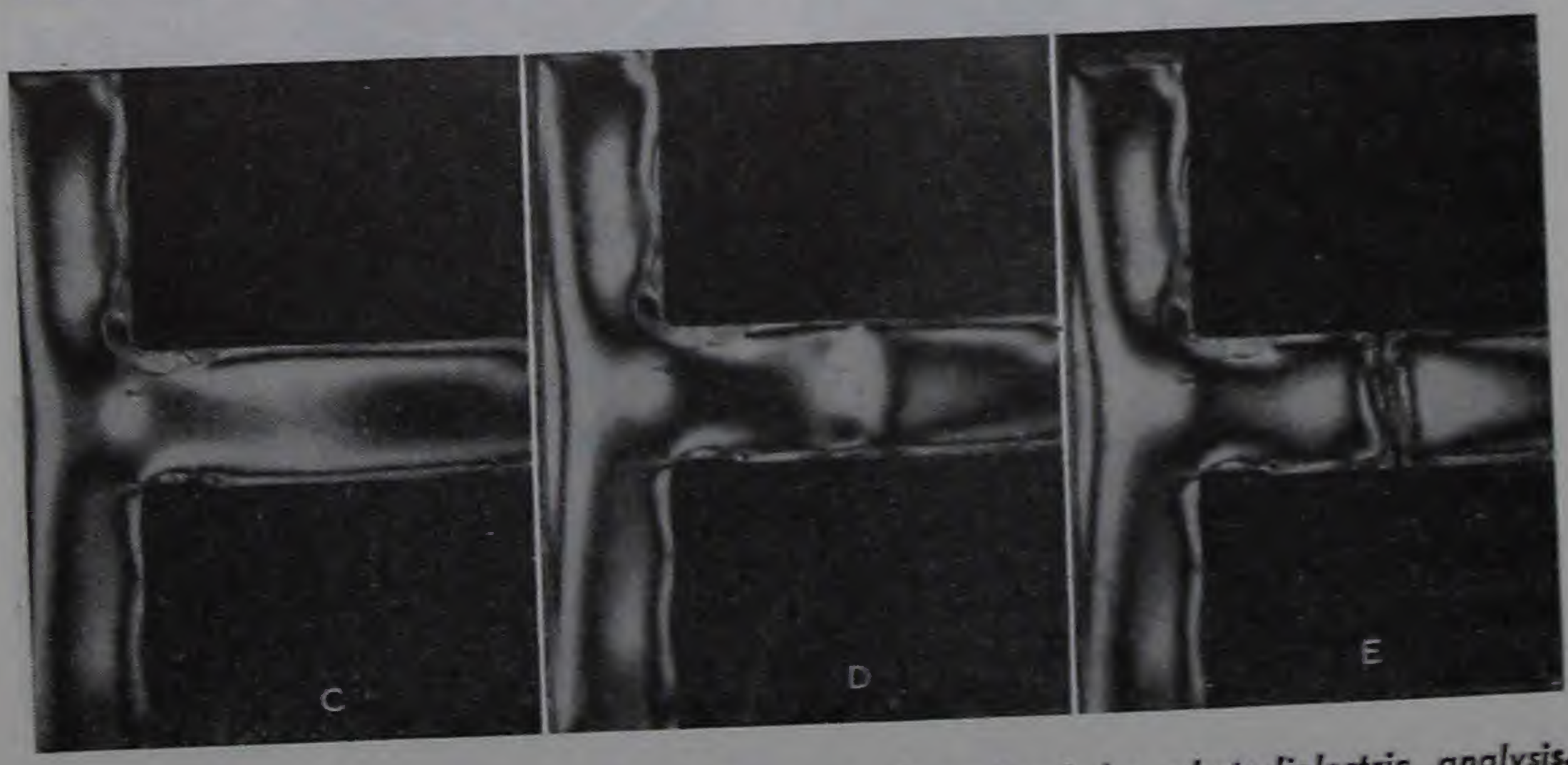


Fig. 65—Three stages of dielectric failure as determined by photodielectric analysis. C—low-voltage gradient; D—high-voltage gradient; and E—after failure. Material is cast phenolic

analysis. Under high-voltage stresses, the disturbance to the pattern in the transparent plastic readily can be observed by optical means. Among significant data which have been observed is the effect of electrode size and shape, and the pressure the electrode exerts upon the solid dielectric. These will influence the dielectric strength readings, though they can be predetermined through photodielectric analysis. Internal physical strains in the electrical insulating member also have been observed to have a bearing upon the direction taken by the passage of current at the time of failure.

Some typical results of photodielectric analysis are illustrated in the accompanying *Fig.* 65. In addition to examination in a plane parallel to that of dielectric failure, interesting results are revealed in a plane perpendicular to the electrodes and the path of dielectric failure.

Chapter IX

Design Principles for Molded Plastic Parts

Molded plastic parts fulfill many useful purposes. From the experiences obtained from thousands of molded parts, it has been possible to establish definite principles as aids to design. These principles are not hard and fast rules, but represent good engineering practices to be followed as long as they do not restrict the utility of the contemplated article. Naturally, departure from conventional practices has its price, but benefits accruing from such departures usually more than offset additional expenditures. It is the responsibility of the designer, however, to decide whether or not it is economically feasible to insist upon a difficult design. Possibly a slight modification for lower mold cost or lower cost per piece will limit the usefulness of the part in question.

While in this chapter emphasis will be placed upon recognized design principles for molded plastics, the reader should not gain the impression that the molding of plastic places a restriction on his creative efforts. Progressive firms should take the initiative in suggesting new fields of applications for molded parts. When the demand is well founded, materials and methods will follow the lead.

Certain features of molded plastics, which have been brought out in earlier chapters, make them highly desirable for engineering designs. These features are tabulated below for convenient reference.

1. Mass production of parts with a high degree of accuracy
2. Unlimited decorative effects and color possibilities
3. Materials are inherently resistant to attack of chemicals and corrosive media
4. Their low heat conductivity makes them comfortable to touch at temperature extremes
5. The transparent qualities of many are unique
6. Combination of complicated metal inserts and inlays into one integral unit
7. Simplification and improvement of machines through the use of plastics as combined structural and insulating members.

During the design of a molded part, the engineer should endeavor to visualize how the piece may be withdrawn from the mold, and should anticipate any objection which the molder may raise. If a clear picture of the molding operation is retained, including removal of the piece from the mold, difficult undercuts will not appear in the design. Knowledge of molding methods and how molds are made are assets to the designer, inasmuch as his designs might eliminate those features that entail costly machining operations on the mold itself as well as costly production operations. General experience rather than specific rules is the best guide for molded plastic design. Nevertheless, there is valuable information that can be obtained from the experiences of others.

Among the laudable features of well-designed molded plastic parts are the following:

1. Well-rounded corners and fillets
2. Adequate and uniform material thickness
3. Thin surfaces strengthened by reinforcing ribs
4. Flash lines requiring a small amount of finishing
5. Design with due regard for flow of plastic material
6. Adequate material about inserts and cored holes
7. Avoidance, unless necessary, of loose pieces in mold cavity, which would tend to retard molding cycle time.

Undercuts: An undercut in a molded plastic part is determined not only by the design details but also by the method of molding and the mold design. Strictly speaking it is a relative term descriptive of some portion of the design that would prevent the direct and simple ejection of the piece from the mold. In former years when straight compression molding was almost universally applied, molders admonished against undercuts that would necessitate costly split molds and retard the molding cycle. Common sense would tell us that this admonition still holds true if there is a simpler and yet satisfactory way of designing a part without incurring an undercut. There should be no restrictions, however, on designs in molded plastics if of necessity they should entail undercuts. Recent developments in transfer molds and injection molds have been prime factors in broadening the scope of design possibilities and in making possible designs that would be impractical in conventional compression molds. Consequently,

before deciding whether a design detail constitutes an undercut or not, the mold design and molding method should be studied.

From the standpoint of conventional molding, internal undercuts are impractical, as shown in *Fig.* 66. On first examination, one would feel prone to suggest a blowing mold using a thermoplastic molding blank. However, if the article is to have relatively heavy walls and be molded of a thermosetting material, other expedients must be examined. While a core of some material that may subsequently be removed by a solvent can be placed within the mold and the molding material flowed around it, the cost and labor of dissolving this member would be prohibitive. Further, induction heating to fuse a metallic internal coring member is possible though costly. For thermosetting materials, a design in two parts appears to be the most practical expedient. Blowing of thermoplastic materials has been worked out with a fair degree of success on equipment resembling that used in the manufacture of glass bottles. Small neck plastic bottles, complete with threads, have been produced from polystyrene and polyethylene. The practical, squeezable features of the latter have offered un-

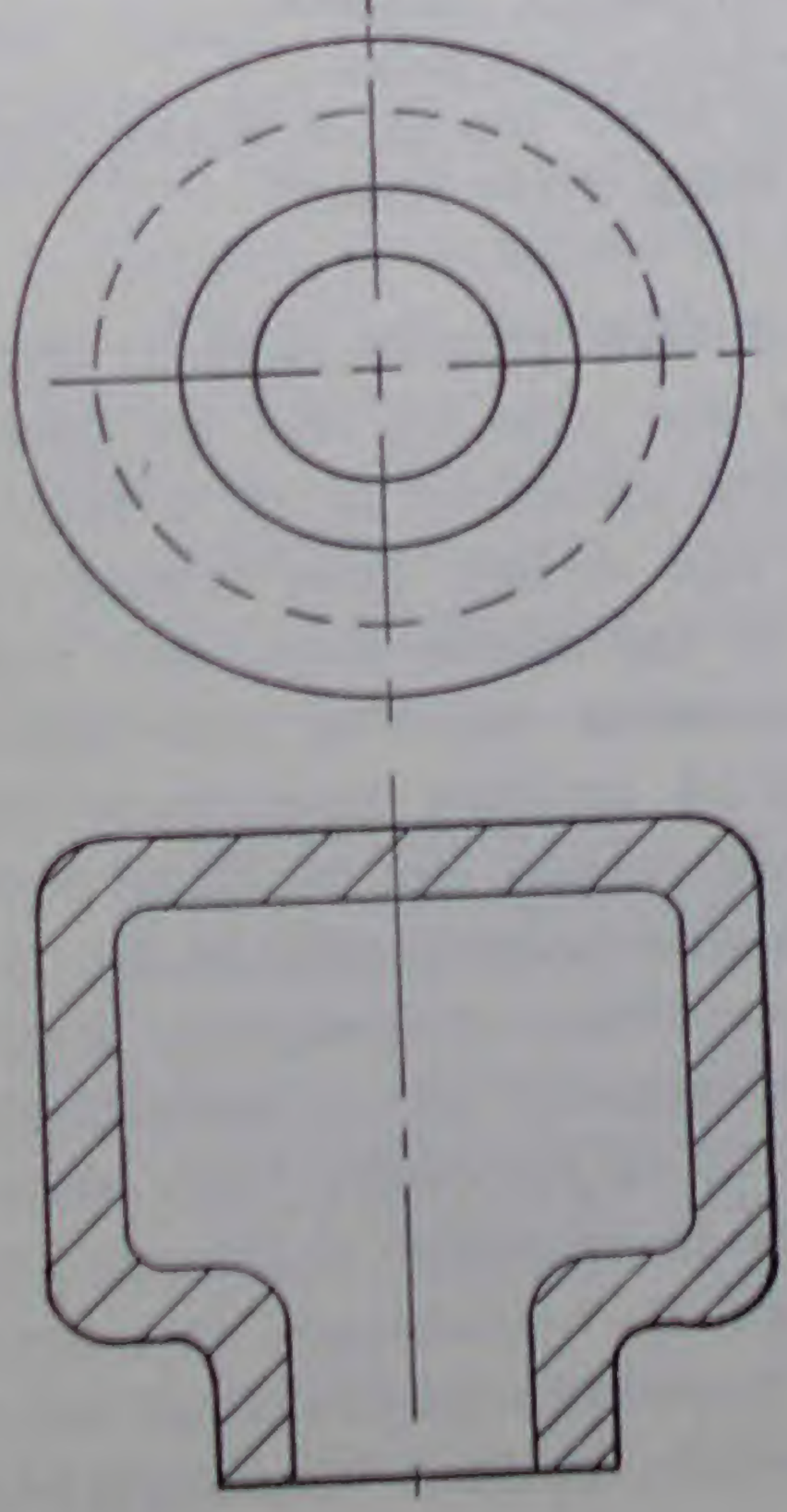


Fig. 66—For conventional molding, internal undercuts, such as shown here, are impractical

usual design possibilities.

If the internal undercut is slight, a split punch may be employed to form the section. The punch is withdrawn with the molded piece, and the elements pulled out one by one.

Undercuts on the outside surfaces of molded articles are not difficult to reproduce, though they usually will entail a split mold or loose mold pieces, see *Fig.* 67. For handling split molds, a tapered chase or side-acting rams may be employed, the former being used most extensively. An article such as the bushing shown in *Fig.* 67 may be molded by transfer or by compression methods. If the production requirements are not large, some relatively simple and symmetrical undercuts may be machined into place. This will save the expense of a more costly mold. Machining operations also can be used to produce internally disposed undercuts which are impractical to mold into place. Further expedients employed in molding undercuts such as may be occasioned by decorative engravings or letters on the side of a housing, are the preparation of loose mold parts or panels detachable from the main part of the mold. These loose mold pieces will come out with the molded articles and can be removed easily and reinserted into the mold cavity.

One enterprising manufacturer, confronted with an external undercut on lettering distributed around the periphery of his molded piece, resorted to the use of a cooling medium directly after molding to chill the article and thereby shrink it by thermal contraction from the undercut in his mold cavity. This procedure is somewhat unreliable when accurate tolerances are to be maintained because of uneven shrinkage and internal stresses that are likely to occur when this method is followed.

In order to take up one further example of the forming of undercuts on molded pieces, an example of a molded cover for a cooking vessel may be cited. While design principles for an economical molding may require restyling to avoid the undercut, such a practice cannot be pursued in this instance. An undercut is required on the knob for the grasp of the fingers. The piece may be molded in a direction parallel to the center line through the knob and cover. This necessitates the employment of loose pieces in the mold cavity to shape the knob as shown in *Fig.* 68. Made in two parts, the loose mold pieces withdraw from the mold cavity together with the molded cover. This is

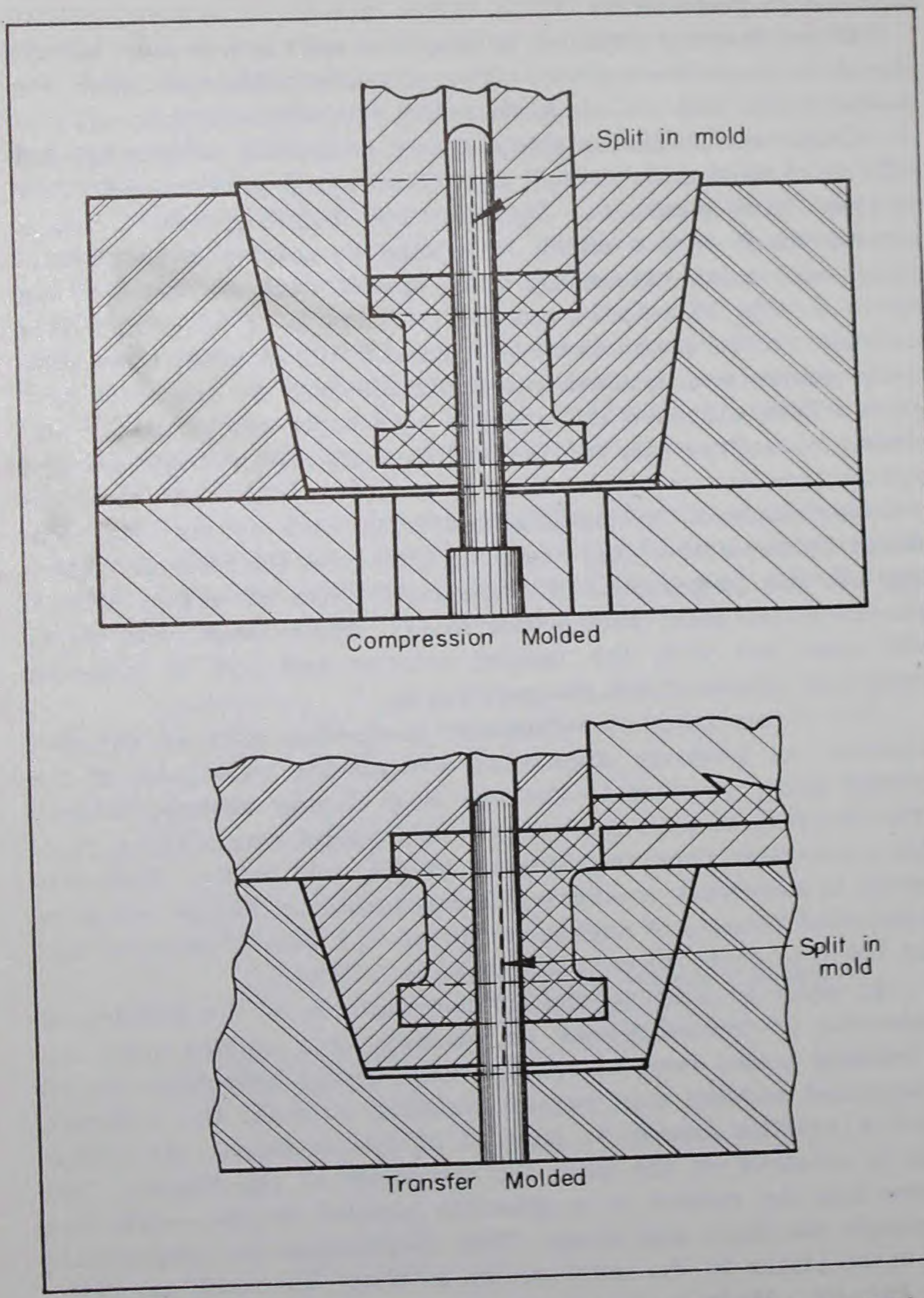


Fig. 67—Undercut on outside surface of part requires use of split mold to permit release of part from mold

another example of necessary undercuts upon molded designs which cannot be conveniently altered on the drawings. Loose pieces in the mold increase handling during molding operations but are feasible in some instances.

Other methods may be employed for molding the knob upon

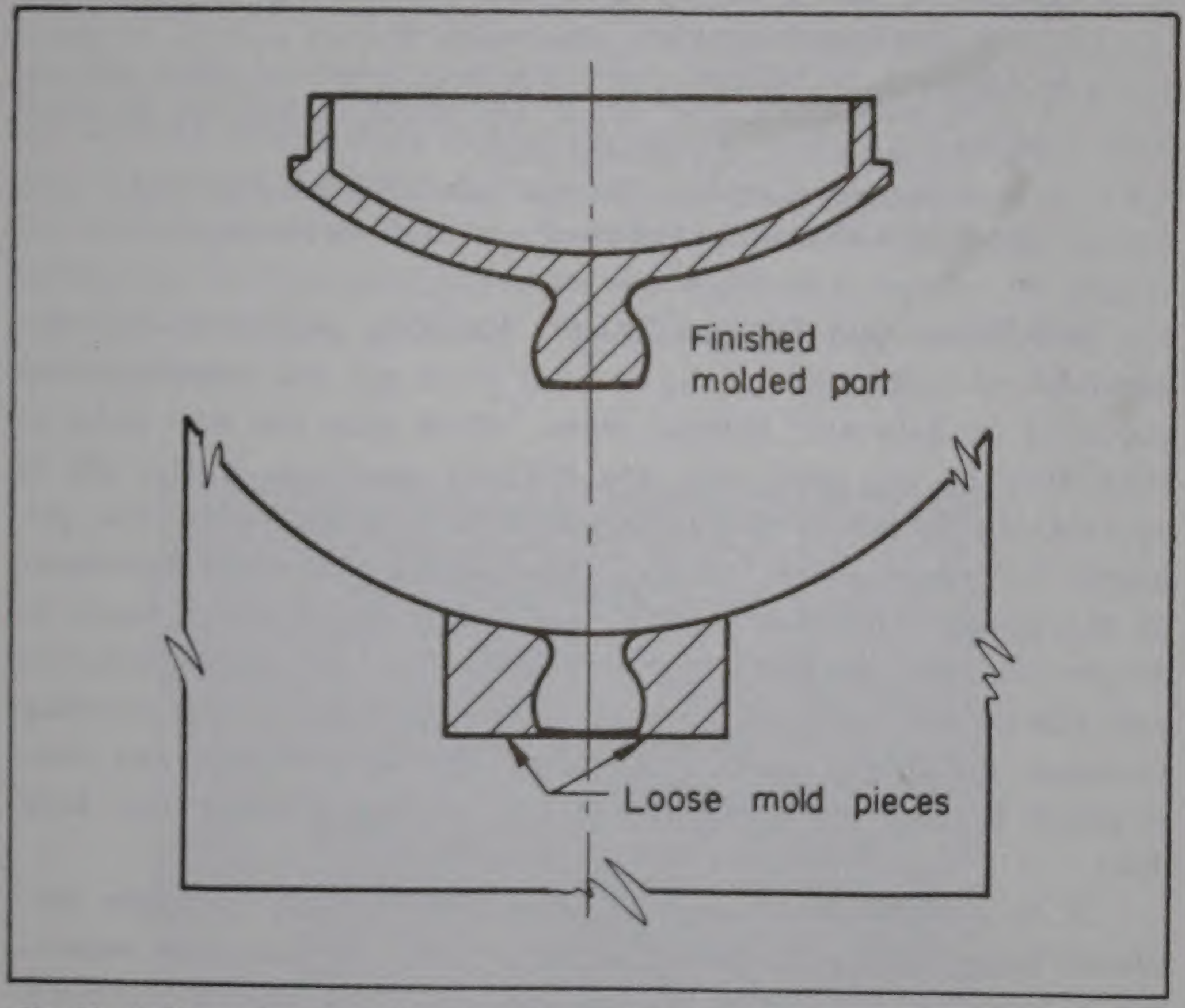


Fig. 68—Molding of cover and knob made possible through the use of loose mold pieces

the all-molded cover. One procedure, adaptable to thermoplastic materials, would mold the knob and cover separately and unite the pieces by some solvent cement along a small recess molded in the top of the cover. Still another would require the knob and cover to be molded in separate pieces, the knob with a stud for attachment through the cover top by ordinary screw machine parts. Finally, if neither of the foregoing operations appear desirable, it is always possible to machine the undercut and to remove the tool marks by buffing.

Reiterating, some of the practices that have been followed

for producing undercuts on molded articles are as follows:

1. Using split cavities, held together by tapered chases or side-acting rams, in a side-angle press
2. Machining undercuts in a separate operation
3. Removing loose mold pieces with the molded part and re-inserting into the mold for the next cycle
4. Molding the article in two parts and uniting through screw machine inserts or cementing operations
5. Adapting to internal undercuts such members which will remove with the molded article and which in turn can be fused or dissolved from the molded piece
6. For shallow undercuts, thermal shrinking may be relied upon in some instances to remove the piece from the mold.

Side Holes and Oblique Holes: Running parallel to the discussions on undercuts in the molded piece are the considerations accorded to side and oblique holes. Core pins for side holes if supported at one end only are difficult practices if the pin is appreciably longer than its diameter. This situation is true primarily for compression molding. During the downward movement of the plunger there is a high pressure gradient which tends to distort the core pin from position. After compression is complete and plastic flow induced, there is a tendency to equalize molding pressure about the mold cavity, but, if the core pin has been stressed beyond its elastic limit, the damage already has been done.

It is obvious that long thin pins will bend as a simple cantilever beam during the compression stroke. By the same reasoning it becomes clear why inserts and core pins placed vertically with respect to the movement of the plunger are preferred in compression mold designs. Such pins have uniform pressure distribution about their periphery, providing they are not too long and will not buckle as a column under load. When side holes are of short length, such as through the sidewalls of a molded radio cabinet, a manually operated pin plate mounted on the side of the chase, can be used to core the holes into position during molding.

Oblique holes as well as side holes, ordinarily are unsuited to molding designs. When their presence is essential, the manufacturer usually drills the holes rather than attempting to complicate the molding procedure. There are some notable exceptions in

molding side holes and oblique holes whereby transfer or injection methods are employed with considerable success. In the molded part shown in *Fig.* 69, not only are side holes and oblique holes placed in unusual positions but, in addition, some of them are on a radius, requiring withdrawal of the mold piece on a radius. The piece is an example of a difficult molding job which would not ordinarily be handled by compression molding. Unusual holes with bends at such a radius that the mold piece cannot be withdrawn, may be formed by low-melting alloys which are removed from the finished molded part by high-frequency induction heating methods. Obliquely placed holes require loose pieces that stay with the molded piece as the force is withdrawn and must be removed before the cavities are placed in the mold once again. A slight taper on the core pins will facilitate their removal from the molded piece.

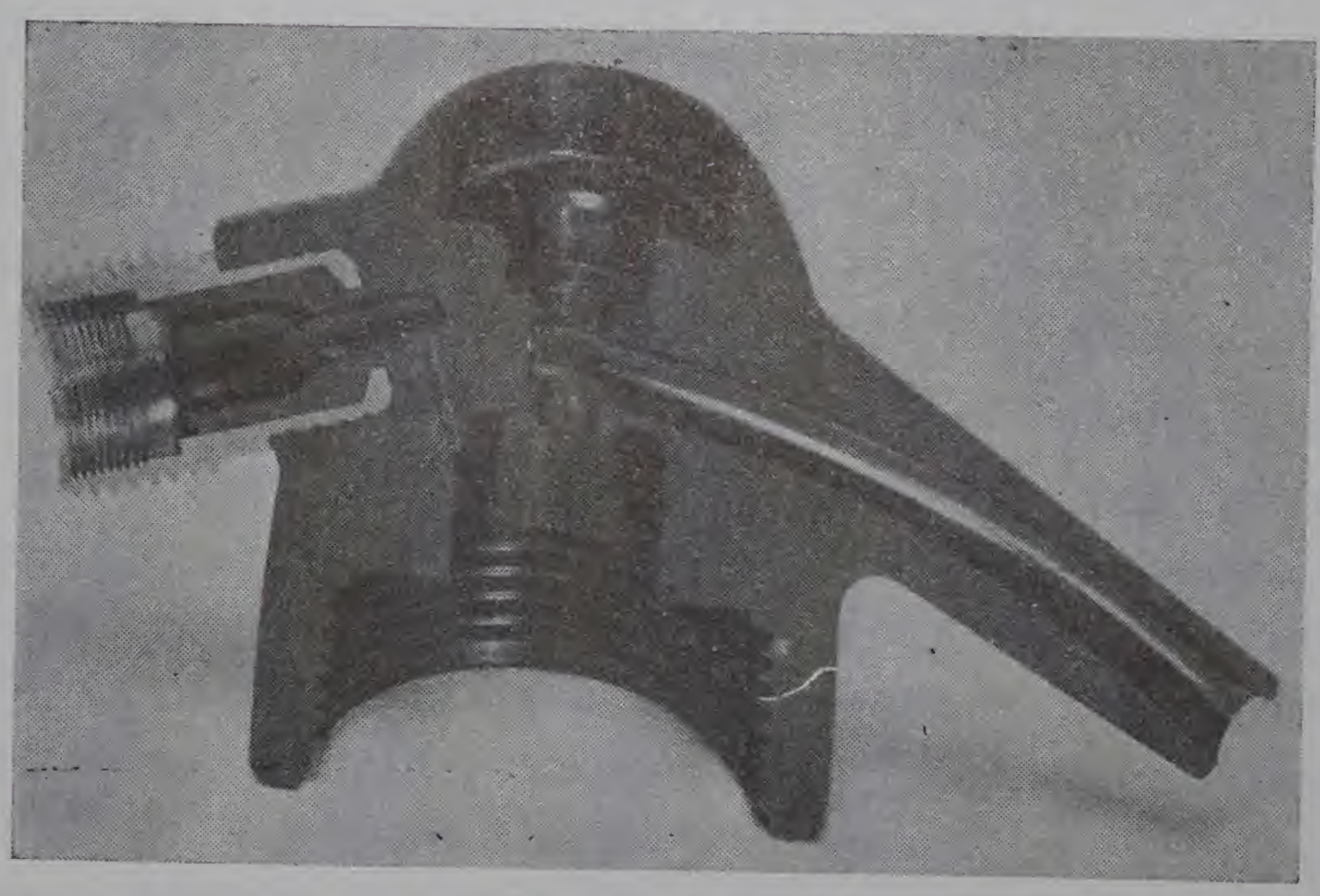


Fig. 69—Example of side cores and oblique holes in transfer-molded phenol plastics

Long horizontal holes, with core pins supported at two ends, have been effectively produced in molded plastic design. The function of the two supports is to prevent displacement of the core pin during the downward stroke of the force. Too long a pin sometimes will result in a slight bowing effect. When a molding composition other than a fabric-filled type is employed, the use of preforms is recommended. Encirclement of the core pin by preforms before insertion into the mold cavity will facilitate rap-

id and effective distribution of the molding material. A design of this description is shown in *Fig.* 70, which was adapted to utilize large horizontal core pins.

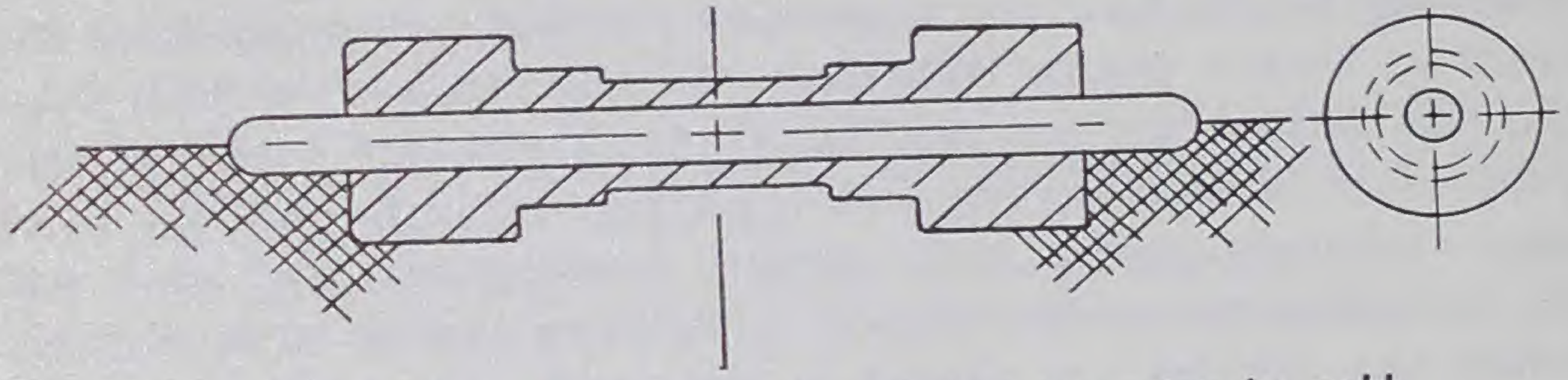


Fig. 70—Horizontal coring pin supported at two points by mold

Location of Holes: The proper location of holes molded by core pins is governed by the flowing qualities of the molding composition and allowable wall thickness. Poorly located holes may not only increase the shrinkage of the molded piece upon cooling but also lead to cracks in the molded piece itself. When the location of the core pin is symmetrical to the onset of molding pressure, and distortion is minimized, deeper holes may be cored. However, for the usual intricate molded pieces, TABLE XLVII should serve as a guide for the proper depth of hole and the minimum wall thickness, with a good factor of safety. It is based upon experiences with present molding materials and is subject to variations in compositions and designs.

Through holes often are specified in the molded part. These offer no difficulty to the molding operation. They may be formed by long core pins which may mate in the mold cavity or a recess in the force, or by butting two pins together. The former method is preferred. A reasonable length of through hole may be estimated as twice D, TABLE XLVII, when two pins butt together. A small flash may occur if the ends are not properly ground flat. This flash is thin and may be knocked out easily. It also is desirable to make one pin larger in diameter than the other to account for possible axial misalignment of pins during molding. During the course of many molding operations the diameter of the pin may wear down, on account of the abrasive

TABLE XLVII

Depth of Hole and Wall Thickness for Intricate Molded Pieces

(In inches. See Fig. 71)

Hole Diameter (A)	Minimum Sidewall (B) Hot Molded	Minimum Sidewall (B) Cold Molded	Hole Spacing (C) Hot Molded	Hole Spacing (C) Cold Molded	Maximum Hole Depth (D)
1/16	1/16	3/32	5/64	7/64	1/16
3/32	1/16	3/32	3/32	1/8	1/8
1/8	3/32	1/8	1/8	5/32	3/16
3/16	1/8	1/8	1/8	7/32	5/16
1/4	1/8	3/16	3/16	9/32	7/16
5/16	5/32	1/4	1/4	11/32	9/16
3/8	5/32	1/4	1/4	13/32	11/16
1/2	3/16	3/8	3/8	1/2	1 1/8

action of the fillers. When the dimensions fall below the tolerance limits, the core pins should be replaced in the mold.

Another possibility for the machine designer is the formation of "step-backs" on the outside contour of molded parts, similar to louvers in radio cabinets and air conditioning grilles. In practice, these holes or cross-openings are produced by the force plug and mold cavity without the necessity of withdrawing core pins or coring plates.

Threads in Molded Parts: The molding of screw threads in plastic materials is quite a common practice. Strong, durable threads are produced, reflecting the accuracy of the mold parts which reproduce them. Either internal or external threads may

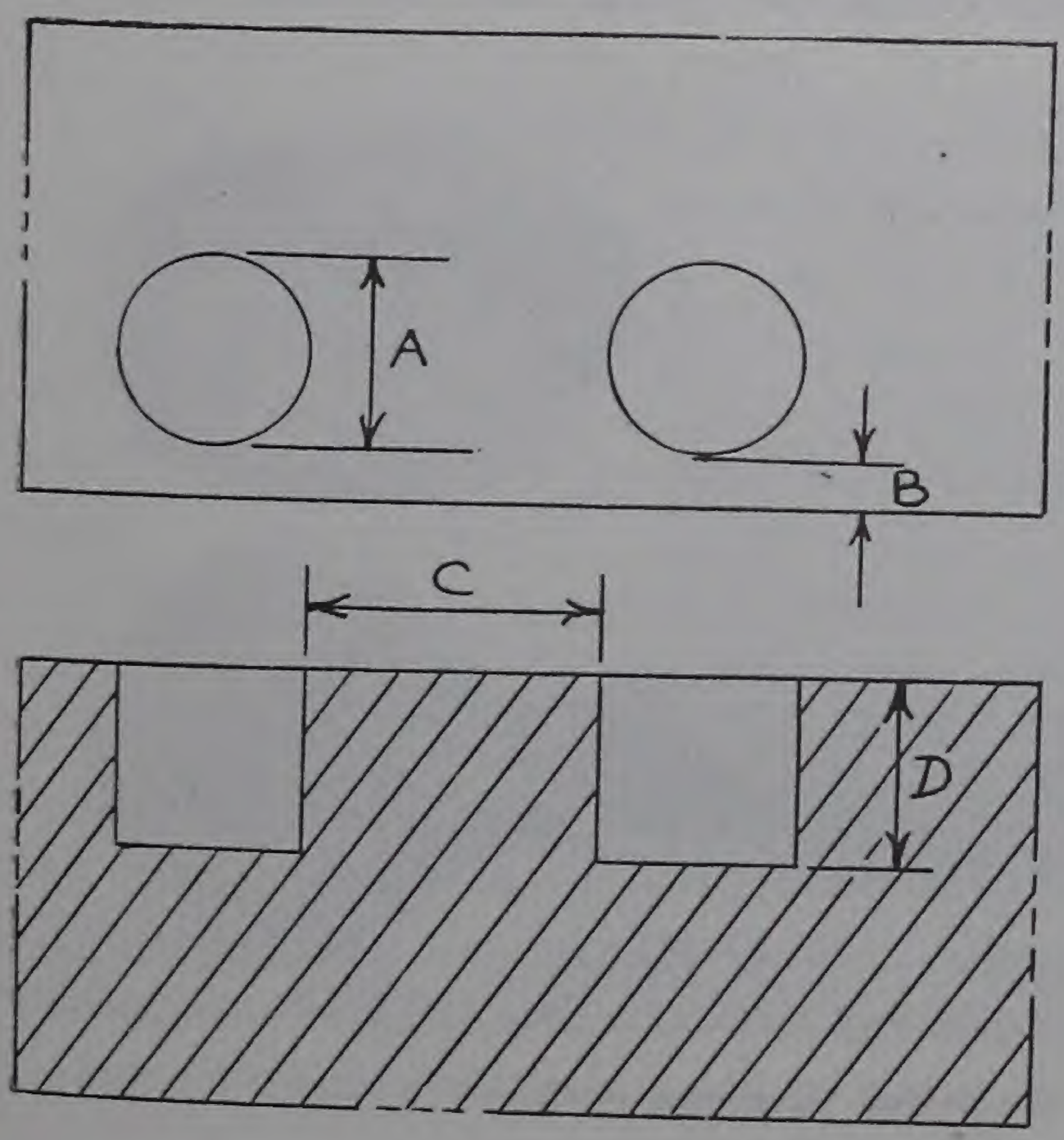


Fig. 71—Recommended dimensions for molded parts (see Table XLVII)

be included in the design, and if compression molding is to be employed, the axis of the threads is located preferably parallel to the molding stroke. On the other hand, threaded components extending in several directions are readily accomplished by transfer molding.

When the thread size is small, say No. 8 thread or smaller, metal inserts are preferred, as the molded threads generally are not strong enough. Threaded metal inserts may also be preferred because they are not subject to creep under stress when tightened during assembly. However, there are numerous threaded parts such as telephone handsets, *Fig.* 72, which have proved successful for many years. External and internal threads are required for this assembly.

For bottle and jar caps which frequently employ molded threads, a special standardized thread has supplanted the standard National-Form thread employed for other mechanical assemblies. This special thread facilitates the removal of caps and enclosures from bottle tops. After molding, bottle caps are unscrewed from the thread forming plugs accompanying the mold cavity. Screw threads for bottle stoppers sometimes are produced in the mold cavity by the hobbing process. The mold will assume the shape of the master hob in every detail. When screw threads are so formed, provisions must be made to allow the master hob to turn freely during pressing, the bearing seat be-

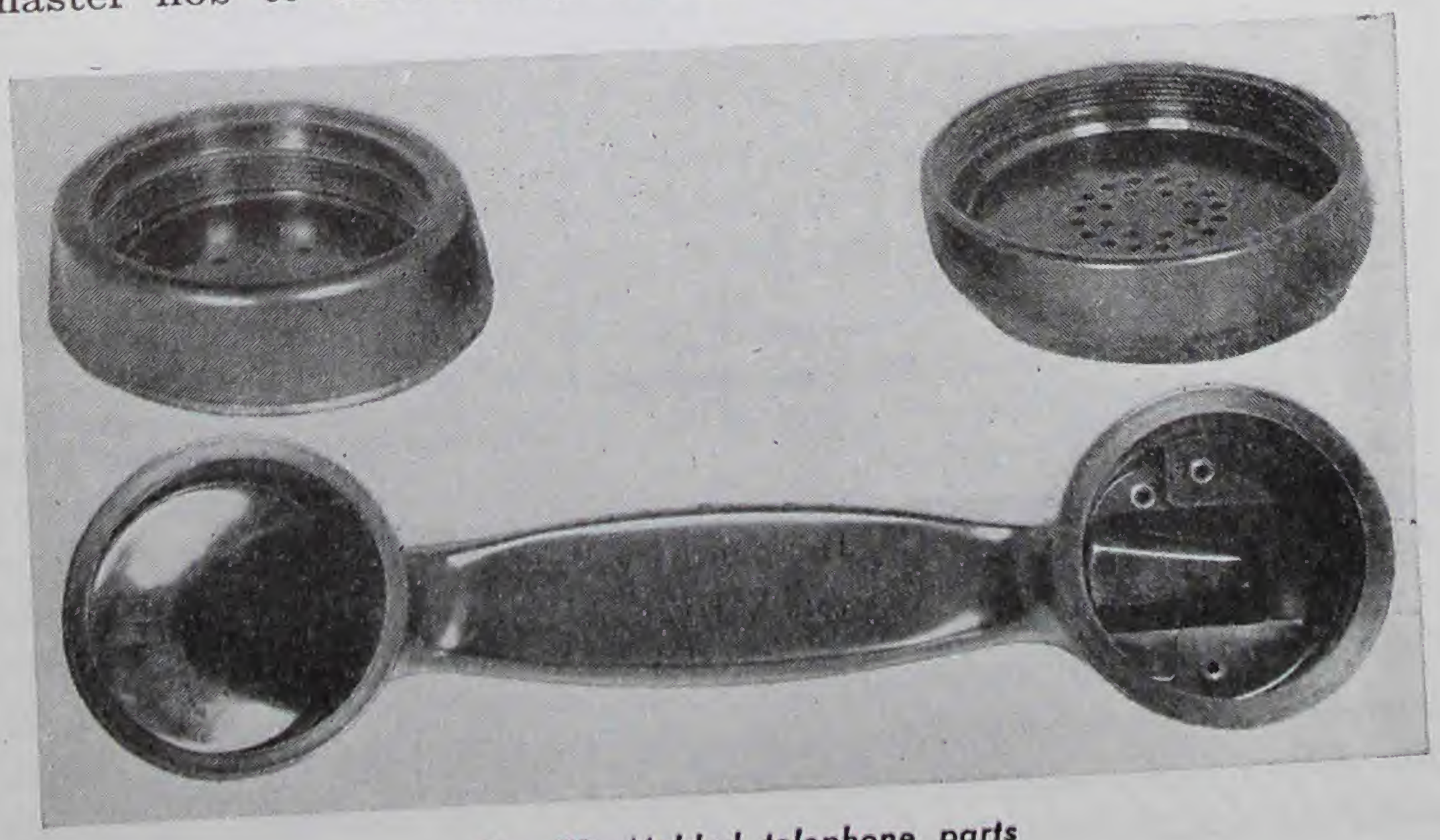


Fig. 72—Molded telephone parts

ing a large, hardened steel ball, capable of rotation under high pressures. However, the thread-molding plugs more often are machined from tool steel.

Various molders have made a specialty of molding small threaded bottle caps, many millions of which are produced every year. To simplify their removal from the mold, various phenolic and urea stripping compositions have been developed, which permit ejection over the threads at molding temperatures without unscrewing the threads. On the other hand, some molders employ quick-acting chucks which will rapidly unscrew the molded caps from the dies. Thus, while one set is being molded the operators may be removing the caps from a duplicate set of punches. In still further refinements, some molds have been designed with complete automatic unscrewing devices. At the end of the molding cycle, an electric motor is started which, through a worm drive, rotates the threaded plugs forming the caps. Care must be exercised in such molds, however, to prevent the molding materials from hampering the mechanical operations of the unscrewing mechanism.

Molded threads are more difficult to produce on fabric-filled and cord-filled compositions, where it is difficult to get the reinforcing filler down to the root of the thread. It is not good practice to specify too close a fit of a plastic thread if it is to be assembled to a metal unit, particularly if after or service-shrinkage may cause binding of the parts.

While solid threaded plugs most generally are employed to form threads in molded parts, it sometimes is feasible to form external threads with a split die, which on opening eliminates the necessity of laborious unthreading. As the mold wears, however, the flash at the parting of the mold halves will grow, and the molder must make provisions to chase the threads to remove the flash.

Outstanding examples of careful designs of molded threaded parts are contained in the National Aircraft Standards, where 37 detail drawings of basic fittings have been reproduced. These fittings include elbows, tees, coupling nuts, lock-nuts, Y's, and a wide variety of threaded parts. These fittings were designed strong enough to withstand the torques of aluminum fitting wrenches. Weight and cost savings were readily apparent in their design and application.

Wall Thickness: The thickness of molded plastic materials is determined not only by the design requirements, but also by the methods of molding the material. When cold material is placed into the mold and conventional compression molding operations are performed, thick sections, say in excess of ¼ inch or more, are avoided wherever possible because it will not only mean more material, but it will also greatly prolong the molding cycle to attain adequate cure within the thick portion. Custom molders have in the past shunned thick sections, particularly when thin-wall partitions are present at the same time. Curing time for molded articles is contingent upon the thickest section and not the average wall thickness. Seldom are thick-molded plastic sections uniformly cured. In fact, upon cutting in half and examining molded parts about one inch in thickness, it is not uncommon to find a crack or some uncured granular material on the inside.

Within the past few years, however, the advent of high-frequency preheating of molding compounds and high-humidity heating, have changed the molders' viewpoint on thick molded sections. Parts many inches thick can be reproduced without difficulty by these innovations. By bringing the material closer to molding temperatures within a short space of time, long times of cure are no longer necessary for thick molded parts. In addition, the polishing and examination of a cross section of a thick molded part prepared in this manner, reveals excellent uniformity of texture.

Nevertheless, whether the part be produced with the aid of high-frequency preheating or not, if there are excessive variations in material thickness throughout the molded part, care must be exercised during cooling to avoid the development of excessive stresses and uneven shrinkage. In fact, an annealing or slow-cooling operation would be desirable for maximum dimensional stability. Dropping thick molded parts into cold water may produce complications. The outside surfaces may freeze and hold dimensions, while the inside is still hot. There will still be some volumetric contraction taking place, resulting in internal strains or cracks. This sometimes is apparent in transparent molded articles.

In the design of deep-drawn articles, such as drinking tumblers or the like, it is considered good design practice to taper

off the wall thickness as the material approaches the flash line (see, for example, *Fig.* 73). In this manner, adequate back pressure will be assured upon the molding material, and hence the attainment of a uniformly dense, acceptable structure.

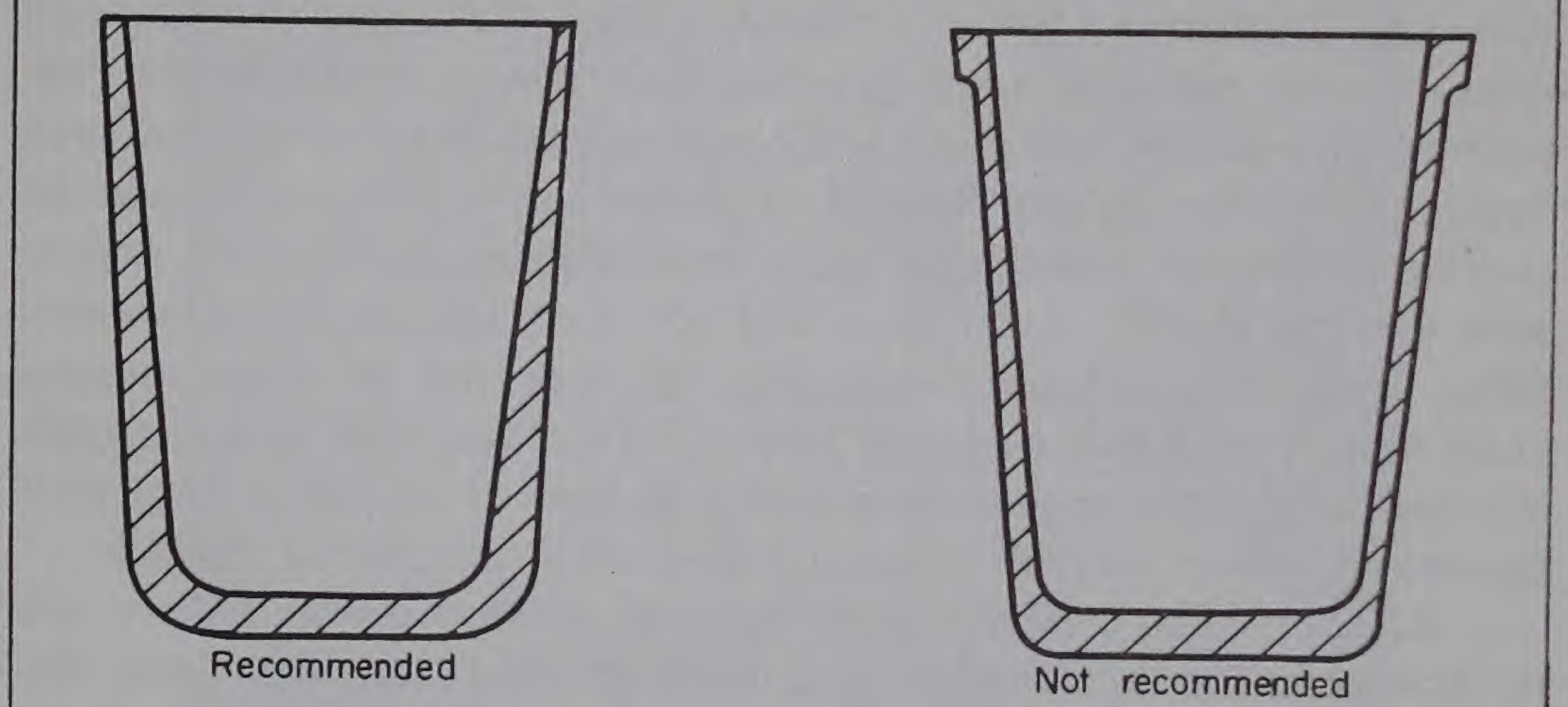


Fig. 73—In design of deep-drawn articles, it is good practice to taper off the wall thickness as the material approaches the flash line

For phenolic and urea plastics, thicknesses for radio housings molded of thermosetting materials vary from 0.093 to 0.156-inch. In general, wall thicknesses for thermoplastic materials run 25 to 50 per cent less. Thin egg-shell walls sometimes appear on pieces to be knocked out, such as the flash formed between a vertical and horizontal core pin, but otherwise, from a sound mechanical standpoint, the wall thickness as cited should be observed. Other expedients exist for increasing the strength of the molded piece without calling for too thick a wall material. These methods require ribbed reinforcements, or metal and/or laminated plastic inserts.

Injection molded parts are limited in their maximum thickness. Shrink marks tend to appear on surfaces of excessively thick parts, due primarily to freezing of sprue and cutting of molding pressure before the molding has completely chilled. Sections

much in excess of ⅛-inch are avoided for most materials.

Several methods are accepted for providing ribbed supports on molded plastics in lieu of extra wall thickness. One method is to raise a slight bead or rib across the surface to be strengthened, while the other requires an outside as well as inside impression in the mold cavity. The former of these designs is shown in *Fig.* 74. In this, the same wall thickness is maintained, permitting not only the same curing time as the unribbed piece, but also allowing a greater strength-weight ratio. An angle of about 45 degrees and generous radii give the best results for a ribbed support of this description. Ribbed constructions may be carried even further—to the production of a rippled surface, analogous to corrugated sheet metal, but such methods are necessarily expensive due to higher mold costs and are not always recommended. Ribs are not necessarily restricted in size for in some designs they may be steep in order to flow sufficient material to some high isolated boss. By employing a width at base of rib one-half of wall thickness, "sink marks" become improbable for thermoplastics.

Ribs provide another advantage in molded parts: They act in the capacity of runners and tend to feed and distribute the molding material. The improved conditions for flow will also serve to strengthen the molded part. For shredded fabric-filled phenolic plastics, where the flowing qualities are not as good as certain wood-flour filled types, thin walls and sharp angles should be avoided in the molded part to promote better flow of material.

Some cumbersome designs from a molding viewpoint may be revamped entirely to give better molding qualities. In the first design of a container, *Fig.* 75, molded for one manufacturer, most of the faults of improper wall thickness were present, as follows:

1. Uneven shrinkage of parts, leading to warpage
2. Long curing time for the thick base
3. Not the best conditions for flow of material.

By correcting the design, the molding time may be reduced to a fraction of the original time and a more uniform, lighter piece is obtained. Exceptions occur, however, primarily when metal inserts are included in the mold, and thicker sections are required to surround adequately the insert with plastic material. This

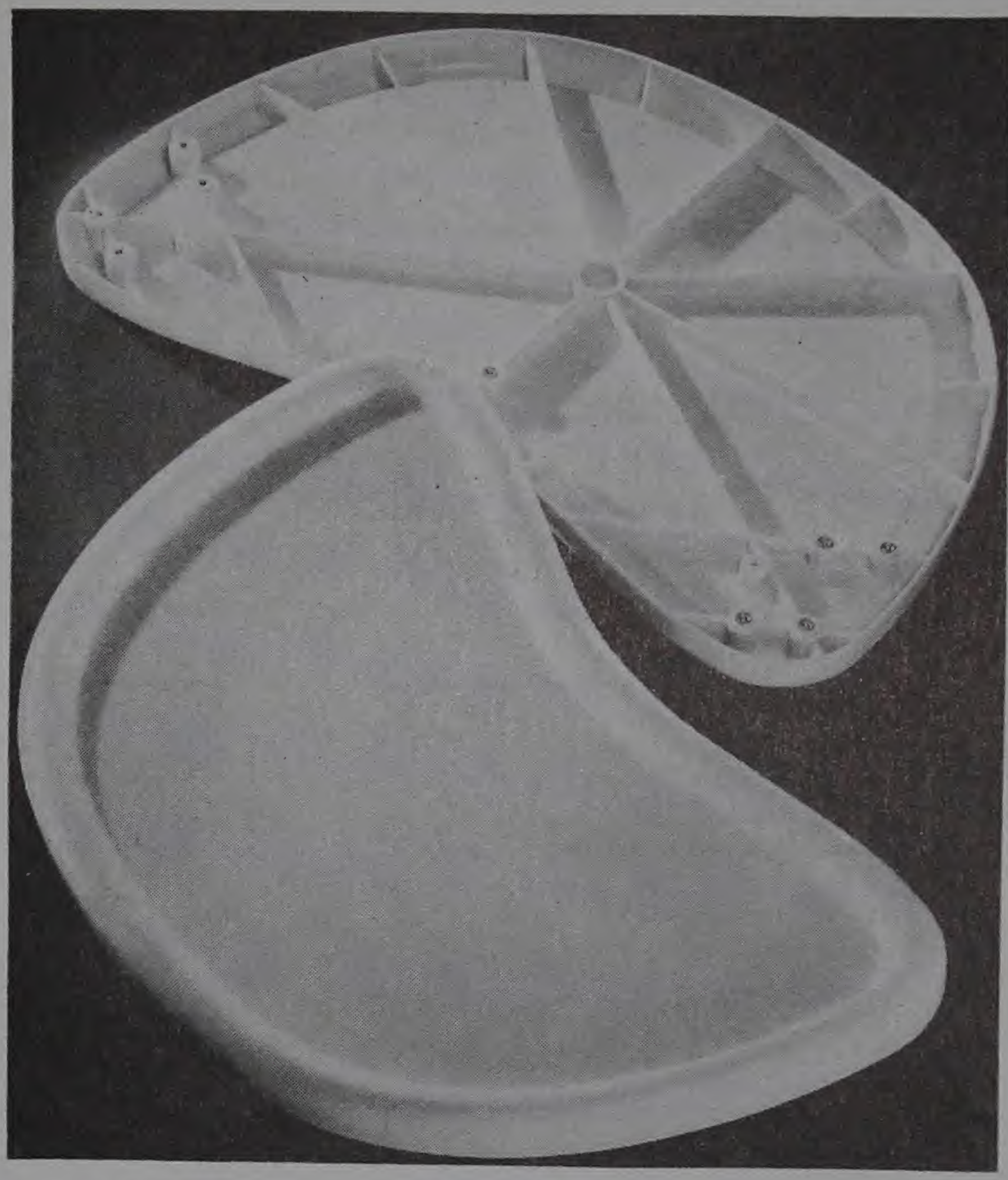


Fig. 74—Large flat areas can be strengthened by ribbing, maintaining uniform wall thickness throughout

instance may be understood readily, by introducing a threaded insert in a corner of the container.

Thin walls in molds as well as thin walls on thermosetting materials are not always recommended. Thin walls in the molds correspond to thin slots in the plastic piece, and even though they may be positioned correctly with respect to conventional molding operations, their presence is avoided where possible. If the thin section in the mold is in the form of a ring, describing some annular groove, conditions are improved somewhat from a mechanical viewpoint as the continuous ring structure will resist distortion much better than a thin, flat, unsupported member. The pressures and pressure gradient developed during the closing of the mold are liable to distort weak mold sections. *Fig.* 76

illustrates an example of what would constitute a weak mold section. The three thin slots running into the housing would require three straïght slabs in the mold cavity. These weaknesses may be overcome by grooving the slots in the descending force so that their engagement will occur before the mold halves come together. However, if the slots were not through slots, and ter-

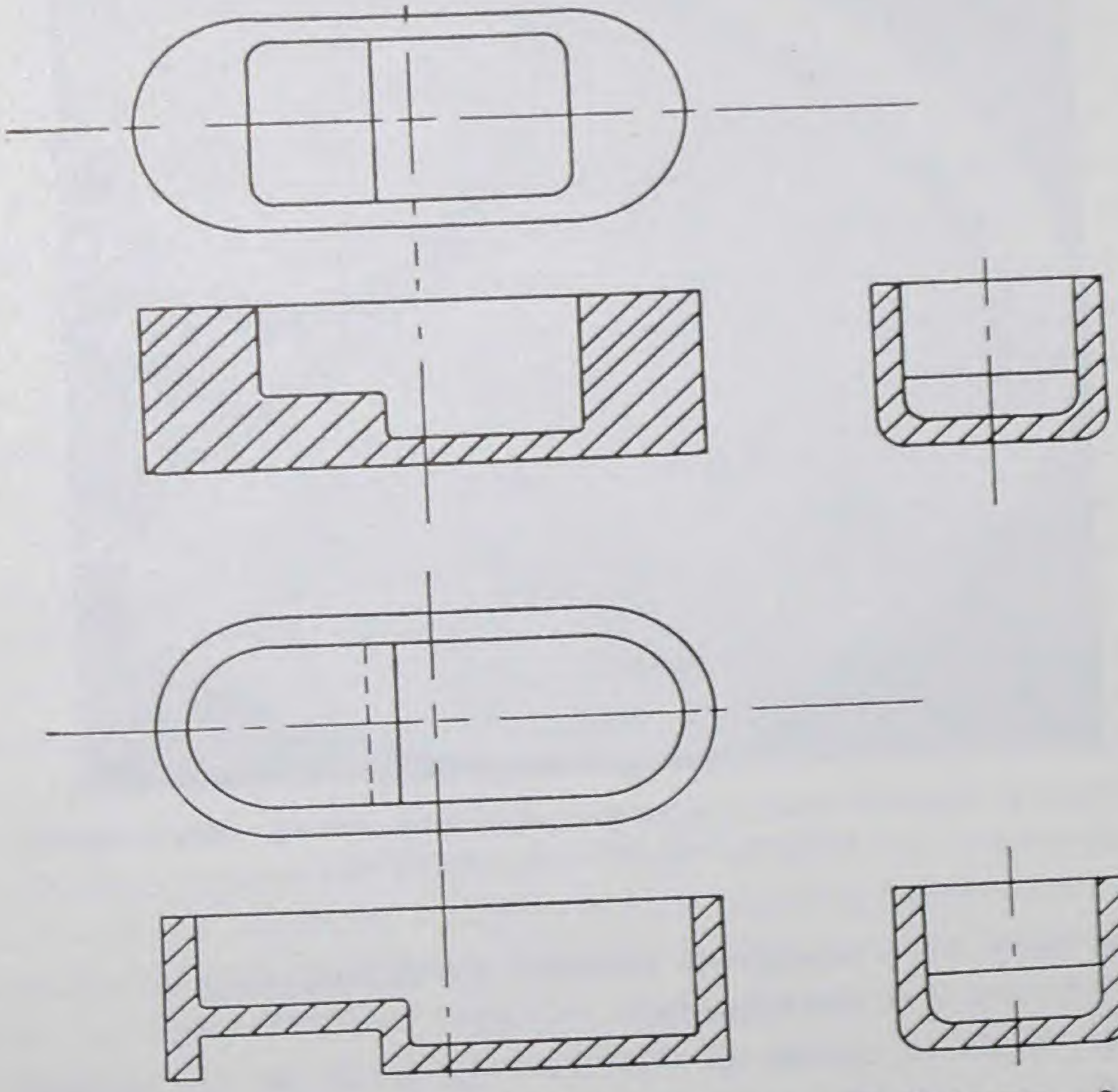


Fig. 75—Container of upper view has improper wall thicknesses. Redesign (lower view) has uniform wall thickness, is molded in less time, has better strength-weight characteristics

minated within the mold piece, the additional support would not be forthcoming. From a design point of view, the problem is illustrative of the fact that the draftsman at all times should consider weak sections in the mold. Generous radii should be allowed for all projections from the mold to strengthen the mold parts and prevent distortion during hardening.

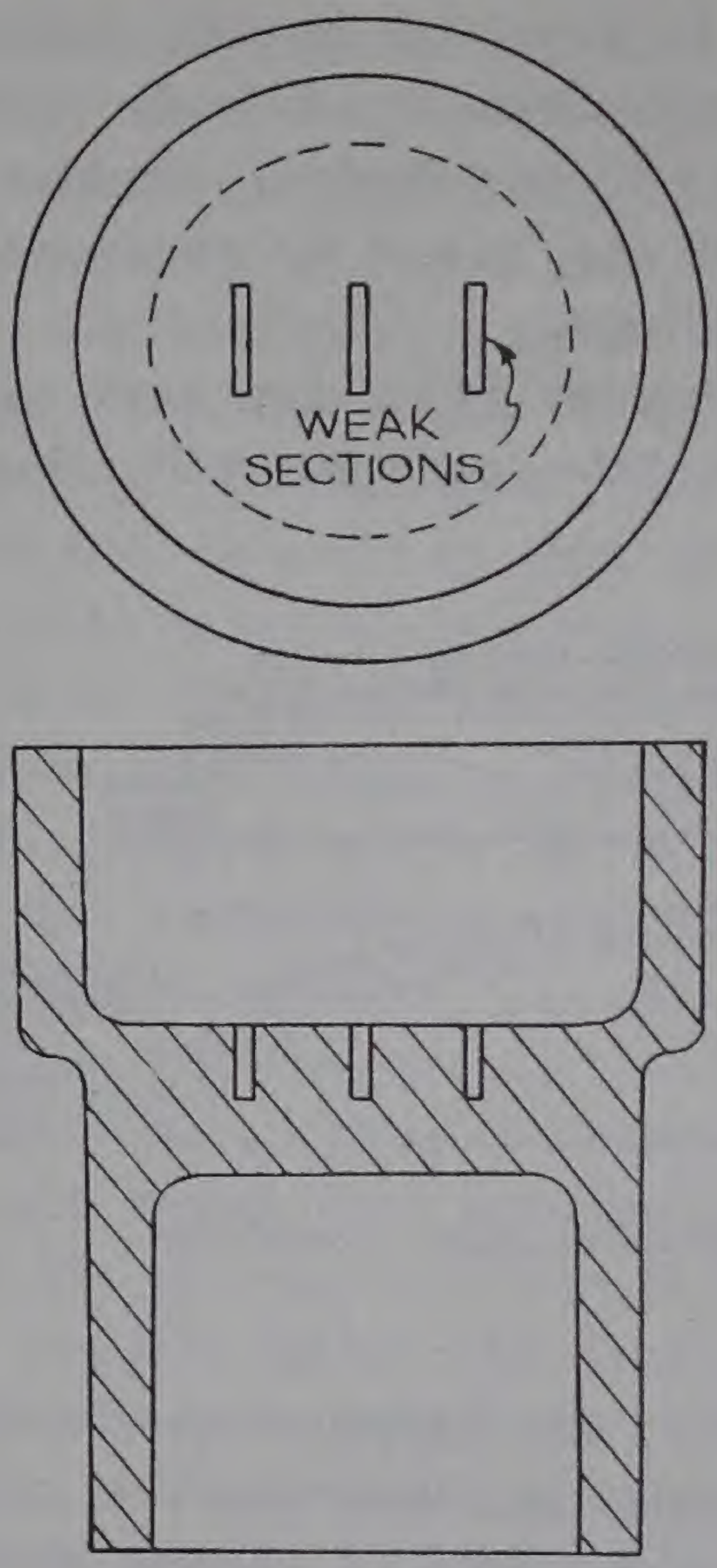


Fig. 76—To mold this piece requires that relatively weak mold members be employed

Molded parts with adequate strength should not constitute an excessively difficult problem for the designer, particularly when good appearance and strong designs run concomitantly. Particular reference is made to the substitution of rounded and domed molded parts, such as shown in *Fig.* 77, for flat unbroken surfaces. The hemispherical shape offers much greater resistance to stress than its projected area as a flat surface. Besides, large flat areas give the illusion of concavity, which only can be counterbalanced by a convex surface. Designs of this nature are suggestive of other ways to improve upon the strength of thin-walled molded parts. Another design feature is also brought out in *Fig.* 77, namely, specifying well-rounded inside corners to avoid dust collection and well-rounded outside corners to avoid sharp edges unpleasant to the touch of the hand.

When molding translucent urea and melamine plastics another design consideration regards wall thicknesses of the molded parts.

Greater shadow or opacity is observed on the thicker sections, deterring to some slight measure from the delicate, uniform, translucent touch of the remainder of the design. Sudden changes in dimensions from thin to thick may show up as darkened lines on the outside of translucent moldings.

The usual molded urea plastic parts are kept as uniform as possible in wall thickness, as this condition will allow a uniform

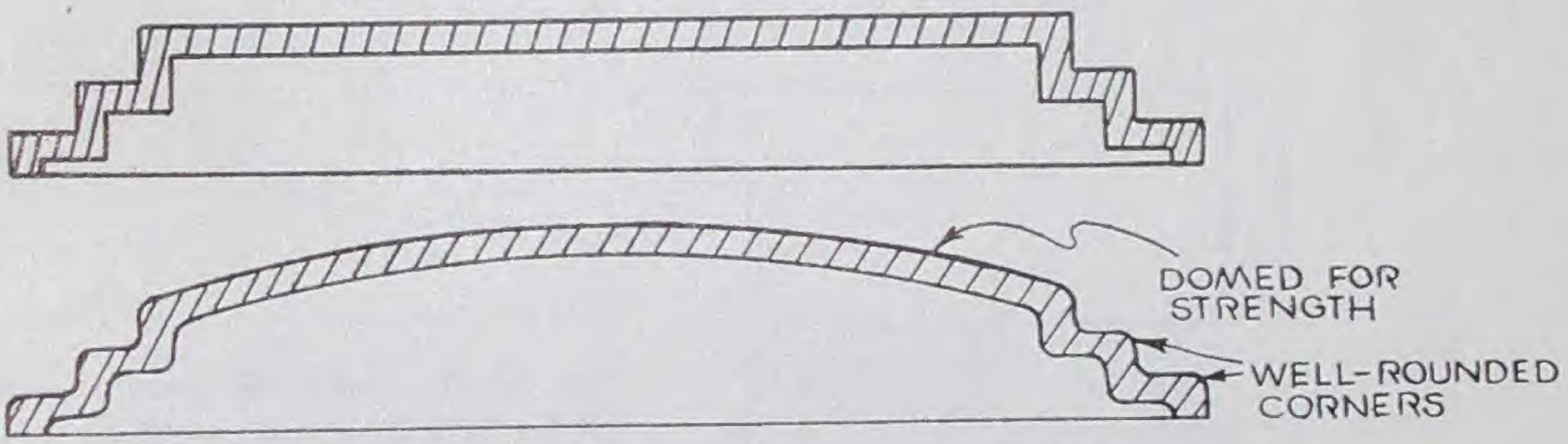


Fig. 77—Hemispherical cover is preferred

curing time, and a decidedly more homogeneous article from an appearance angle. Thick walls in urea plastics are not desirable for molding operations, and a limit of ¼-inch should be maintained in the usual designs. A typical application of molded urea plastics is the light reflector bowl which has become so popular. The wall thicknesses of these range from 0.040 to 0.100-inch.

In the design of molded urea and melamine housings with relatively deep draws, best results are obtained with a thinner section at the top of the draw than at the bottom. For example, some housings 6 inches deep are specified with a 0.080-inch wall thickness at the bottom and a 0.070-inch wall at the top. Experience has shown that the best moldings in urea plastics are produced with a decreasing wall thickness toward the flash line.

Location of Flash Lines: After the designer has made progress with his preliminary layout of the proposed molded plastic part, the question of where and how to include the flash line will arise. In general, it is a function of all good molded plastic designs to locate the flash line in as inconspicuous a location as possible. Concealment of the flash line is not always possible, inasmuch as it usually appears across the greatest dimension of the molded piece cross section, perpendicular to direction of molding.

It is considered good practice in some designs to establish arbitrarily the flash line by including in the design an additional rib which would lend itself readily to buffing. Wavy and irregular surfaces upon which the flash line would be difficult to buff properly, should not harbor any mold parting lines. Likewise smooth, lustrous flat areas can also be marred by a mold parting line down the center. On the other hand, by redesigning the housings or container with a bead or ring about the bottom periphery the flash line can be removed to a sharp corner with comparative ease.

Location of the flash line at a straight, sharp edge is a good feature. Otherwise finishing operations are required at parting lines on well-rounded corners to reduce the fin to the same smooth contour of the rounded section. Not recommended and recommended designs illustrating this principle are shown in *Fig.* 78.

Other fins may appear in the thin interstices between split cores in mold construction. These fins are contingent upon the accuracy with which the machining operations have been conducted, and the closeness of the fit between pieces as well as the mechanical support given the mold to prevent spreading. Side holes, which are formed by core pins and extend through to vertical molded cavities, have flash lines at the area of division between the two cavities. Thickness of flash lines vary from 0.002 to 0.015-inch, depending upon how long the mold has been in use. Flash lines on well designed transfer or injection molds may be negligible. This is possible in these cases because molds are tightly closed before material is introduced.

Location of Gates: While the location of gates in injection molds often is considered a problem of mold design, the designer concerned with the maximum strength and best appearance of the molded article should consider certain peculiarities of injection molded articles. When the molding material is forced through the gate into the closed mold it will first flow out fanwise from the gate entrance, and then double back on itself to fill out the cavity. The angle formed by this initial fanwise flow can be detected in certain molds involving a long distance of flow, because when the molded piece is broken a line of fracture often will appear along the sides of this angle, indicating imperfect welding of materials at this junction. Better understood are weld marks appearing in injection molded articles, which arise when the material separates at some obstruction in the mold and at-

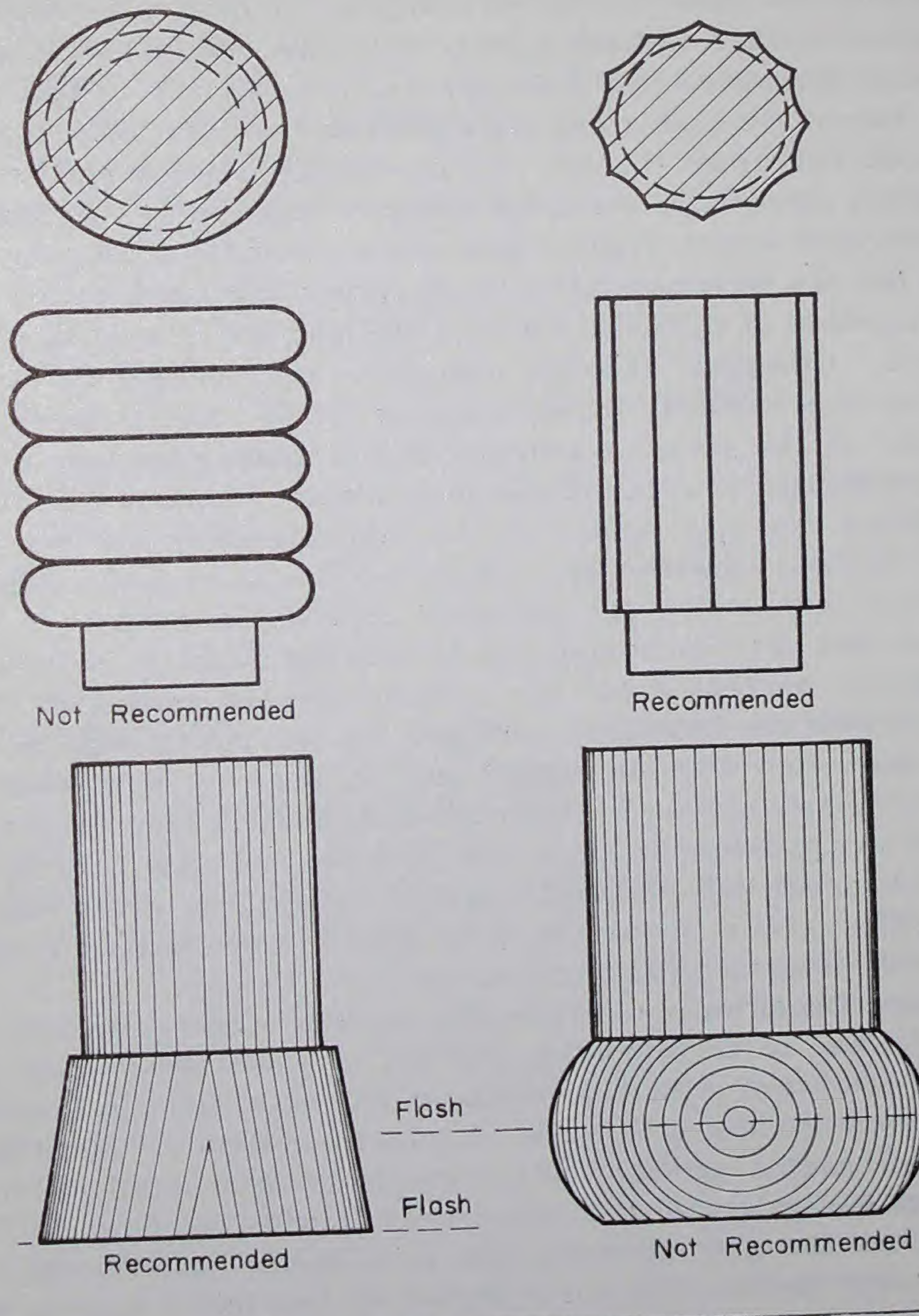


Fig. 78—Finishing operations to smooth off fins are simpler on parts where flash line occurs on a straight, sharp edge

tempts to reunite further on. These weld marks represent points that are structurally weaker than the rest of the article.

In general it is the practice of mold designers to locate the

gate or sprue at the thickest portion of the molding. In many examples more than one sprue will give best results. Location and design of sprues are discussed in greater detail in the chapter on injection molding.

Curved Edges and Fillets: Though sharp corners and clean lines are attainable in molded plastics, there are many advantages accruing from the use of generous radii and fillets in the designs. These advantages are manifested by:

1. Improvement in flowing qualities of the molding material
2. Greater strength in the molded part, because of the more gradual change in dimensions, with diminution in stress contration
3. In some instances, less hand work upon the mold, the radii formed by milling cutters establishing the finished dimension
4. Less accumulation of dust in sharp corners
5. More pleasant to the touch of the hand
6. Sometimes an improvement in appearance of the external design feature
7. Minimizing the possibilities of chipping and marring of sharp molded corners
8. Minimizing wear of sharp edges in mold by the molding compounds
9. Less chance for dust accumulation.

With advantages such as these, it is no wonder that molded plastics emphasize well-rounded edges on the internal, as well as the external surface of the design. The one largest exception to the use of curved edges and surface is the location of the flash line, which is best designed on a sharp clean edge. This simplifies the finishing operation. Aside from these exceptions curved surfaces and edges in plastic design are useful expedients.

The gain in physical strength of the molded plastic parts and the gain in strength qualities of the mold itself by good radii and fillets are important. While it is an impractical procedure to establish a standard limit for all molded plastic pieces, reasonable care may be exercised by specifying at least 1/32-inch for all corners, and more where preferred by the designer. The general expression, "break all corners", sometimes will suffice and leave the selection of the proper radii to the toolmaker. Sharp corners on inside construction frequently are circumvented or crossed by fillets or ribs, designed to promote better flow to the more remote

parts of the design. Filling out large molds with thermosetting resins requires artifices of this nature. Thermoplastic materials are better in these respects, due to better flowing qualities during the molding operation.

From an appearance point of view, the elimination of dust traps on outside crevices on molded plastic parts is a worthwhile feature of molded plastic design. Too often this fact has been overlooked until the molded part has seen some actual service. At least 0.032-inch should be allowed on inside radii for dusting purposes. Though sharp, clear lines augment the beauty of some designs, the general tendency has been to soften the designs with smoother curves. Prevention of chipping of corners because of impact and smoother handling of the piece have been two good reasons for this trend in design.

Consistent with curved edges in plastic design have been the broadly curved surfaces of plastic housings. This feature is brought out in greater detail in Chapter XXIV. It serves to illustrate modern and advanced design possibilities in plastics from an artistic point of view. The dual role of the attractive ribbing on recently designed radio housings has not only enhanced the beauty of the sets, but also has served to eliminate and conceal any possible flow marks in the piece.

Flow Marks: A sudden change in the path of flow of plastics as well as a fluid medium involves a loss in energy. In the more sluggish plastic medium, this condition may appear in the guise of flow lines, indicative of the lack of a harmonious flow of material. Effects obtained like this in molding operations may be detrimental to the appearance of the final article. The designer should learn to anticipate and to avoid them by detailing generous radii at the junction of the two sides of a molded plastic piece. Sharp corners obstruct the free flow of plastic material with a weakening of that section, while the optimum design specifies full-rounded corners. Concealment of flow marks on molded housings sometimes is possible through a series of effectively placed external ribs. In general, flow marks are occasioned by improper fusion and blending of molding material. Greater plasticity of the material at the time of flow and any details in the design tending to improve flow about obstructions in the mold, will help eliminate flow marks.

Flow marks may not be readily observed in the more opaque

thermosetting plastics at first, but on aging and in the presence of moisture, may grow progressively worse. Flow marks or flow lines, as they are sometimes called, are more apparent in translucent or transparent injection moldings, requiring care in adjusting the molding cycle to eliminate them. More difficult to eliminate is the weld mark formed when two paths of flow reunite in a mold extremity after they have cooled. Weld marks are discussed again in the chapter on injection molding.

Draft: Allowance for draft or taper is an important design detail for molded plastics, if the piece is to be withdrawn or ejected from the mold cavity. There are no precise mathematical formulas to indicate the amount of draft to allow on a molded piece. Experience has shown that if the piece is withdrawn from a highly polished mold, less draft will be required than if a rough finish is present on the mold surface. Further, the thinner the wall section and the more rapidly the hot mass of molded material will cool, the less the draft angle between the molded piece and the outside mold. However, for general design work a draft of 0.005-inch per inch has proved satisfactory for hot-molded plastics, and about double that value for cold-molded phenolics or bitumen-base compositions. When long draws are involved, drafts of as little as 0.001-inch per inch have been specified with satisfactory results.

Lettering and Engraving: Little has been said heretofore regarding the best methods and proper design principles for lettering and engraving molded plastics. In general, several methods currently employed with appreciable success are:

1. Metal inlays of letters or decorative strips
2. Raised letters and raised designs on the molded piece
3. Sunken letters and engraved designs on the molded piece
4. Letters or decoration mechanically rolled by dies into the molded plastic housing
5. Miscellaneous decalcomania, branding, labels, etc.

Metal inlays should not be overlooked in considering decorative and instructive details on molded plastic housings. Injection molding about die castings with attractively placed metal inlays upon the outside surface, have been the subject of a recently modeled hand stamping machine. Equally attractive inlays in contrasting colors often are desirable, not obtainable by other means.

Raised letters or designs in the finished product require the engraving of the letters in the mold in bas-relief. This operation, while requiring the handiwork of a skilled artisan, is less costly than intaglio or raised letters in the mold to produce sunken letters in the molded piece. On large molded sections where engraved details and lettering are spread out over a considerable area, the pantograph duplicating machines are invaluable for fast and rapid reproduction of designs.

Raised letters, produced by engraving in the mold surface are effective methods of identifying the name or brand of the machine. However, they must not interfere with the removal of the piece from the mold or necessitate a split mold unless absolutely necessary. It is surprising how little the letters need to be raised on the molded product to catch sharp highlights and stand out in bold relief. At the most, 1/64-inch in height is all that is necessary. Decorative trimmings, decorative ribs, and fluting do not require any greater heights for attractive display. Little relief is required to make the surface effective, particularly when good finish, high gloss, molding qualities are prevalent. Lightly colored plastics, however, require slightly higher letters to obtain better distinction.

Molded parts produced from multiple-cavity molds usually exhibit sunken letters rather than raised letters. This is possible only through raised letters in the mold cavity produced by a master hob with sunken or engraved letters. Sunken letters in the molded pieces may readily be filled with lacquers. Air-drying lacquers are used to augment the appearance of the lettering and afford a contrasting color. The thickness and depth of the lines seem even greater with the color pigment present, which is wiped off of all surfaces but those actually forming part of the decorations.

Another popular method of preparing letters for molded buttons and dials for business machines is the two-color molding technique. The letter or numeral is first molded in a light color. This is inserted into another cavity, and about it is molded a second contrasting color, producing a highly readable, permanent symbol.

Molded letters and decorations on plastics are permanent, incapable of being destroyed unless the piece is willfully demolished. This is an important factor when considering that the

attachment of decalcomanias or nameplates does not represent a fully permanent job. Though the latter will reduce mold costs appreciably, choice cannot be made until the merits of the individual applications have been studied carefully. Among other identifying methods used by some manufacturers are those involving the impression of a design by a hardened die into the surface of the plastic to give some identification to the piece. The plastic part must be well backed up on both sides to avoid cracking due to the pressure of the die, though heating the die is an aid. Small dies of this nature are used for registering numbers on plastic housings prior to their introduction to the assembly line.

Knurling is another design principle in the hot molding of plastics. It is used most broadly on small, portable hand machines with all-molded plastic housings to improve the hand grasp on the piece. Another advantage accrues through the use of a knurled surface—concealment of the mottled coloring which generally accompanies parts molded from shredded fabric, phenolic molding compositions. Straight knurls are preferred for small mold parts, though diamond knurls may be used.

The foregoing design principles and features of molded plastics outline in a general manner their design possibilities and limitations. There are no established rules or laws, and to apply plastics properly one must be familiar with the material, from a chemical as well as a molding standpoint. Certain expedients in the design principles have been useful to various manufacturers, and these should be an aid to design work. Some of these have been illustrated and should be suggestive of methods for undertaking new problems.

Allowable Tolerances

Designers are prone to call for closer tolerances than actually are needed. While these tolerances usually can be furnished, it is sounder economy to be as liberal as possible in the design. Among tolerances which usually must be maintained are those that have to do with the relative spacing of metal inserts, which may be locating positions for some stiff metal members. If mold shrinkage, for example, has shortened the distance between two metal inserts which are to serve as a support for a single piece that has been drilled correctly, or blanked out as far as insert location

is concerned, the molded piece may have to be rejected if the inserts are too close together. One method of handling this problem is to remove the piece directly from the mold, and while still hot, attach the piece directly upon a fixture that has locating pins correctly positioned in accordance with the desired tolerances. The locating pins will engage the proper holes or inserts, which have been molded in the correct position, and in cooling the rigidly built fixture will maintain the desired spacing between the holes or inserts in question. Cooling the molded piece within the mold is another expedient sometimes employed for thermoplastic materials.

Some designers have found it possible to maintain close tolerances on overall diameters of round or cylindrical parts through the use of metal or fiber inserts which protrude beyond the molded parts. For example, a metal ring insert may be molded on the inside of a tubular housing at a position where accurate dimensions must be maintained. The tolerances of the metal ring are much closer than that obtained through any molding operations, and any accurately machined piece that is to be pressed into place will fit tightly without setting up undue stresses in the material.

Very exact tolerances are difficult to maintain in molded plastics for the following reasons:

1. Thermal contraction coefficients of plastics differ from that of the steel in which they are molded.
2. Volumetric shrinkage which normally takes place in thermosetting materials while they are being cured is only partly compensated for by the molding pressure. Shrinkage due to cure and due to differences in expansion coefficients with the steel is expressed as the mold shrinkage value. For general purpose phenolic material this may be 0.006 to 0.009-inch per inch, or 0.003 to 0.005-inch per inch for heat-resistant grades. More complete tabulation appears in the chapter on the thermal properties of plastics.
3. After-shrinkage or service-shrinkage may approach the values of mold shrinkage. High temperature operation expedites this after-shrinkage. The after-shrinkage of representative thermosetting plastics is illustrated in the chapter on thermal properties.
4. Unequal rates of cooling of different portions of a given molded plastic article may contribute to the development of internal stresses and dimensional inaccuracy.
5. Method of constructing a mold will influence the tolerances obtained. In fact, the experienced molder knows that how

the mold is machined or hobbed is dependent upon the tolerances specified in the design.

6. Molding methods also influence the tolerances. Better tolerances usually are possible in transfer or injection molding than conventional compression molding. Where thick sections are involved, better accuracy will be maintained if materials are preheated by high frequency methods.
7. Mold wear will bring about changes in tolerances. Many tens of thousands of pieces generally are turned out before any adjustments are made, though during this time, depending upon the steel and the material, the mold and its coring pins will wear slightly—perhaps enough to alter close tolerances.
8. In compression molding the specification of tolerances is dependent upon the relation the dimension holds to the line of molding pressure. Parallel to the line of molding pressure, the part dimension is subject to the amount of material added to the mold and the thickness of the flash line, and tolerances may well be plus or minus 0.005-inch per inch. On the other hand, perpendicular to the line of molding pressure reflects the accuracy and experience of the tool maker, and tolerances of plus or minus 0.002-inch per inch are not uncommon.

Representative tolerances to allow on molded parts are shown in Table XLVIII.

TABLE XLVIII

Standard Tolerances

Type of Material	Method of Molding	Plus or Minus Tolerances — Tolerances (in.) on One Tool Part for Diameters of 1 in.	3 in.	5 in.	Tolerance (in.) on Linear Dimension for Cavity Depth of 1 in.	3 in.
General-Purpose Phenolic	Compression	.0045	.0072	.010	.008	.012
High-Impact Phenolic	Compression	.0055	.008	.011	.010	.014
Cellulose-Filled Urea	Compression	.007	.011	.015	.010	...
Polystyrene	Injection	.0037	.005	.0065	.004	.007
Cellulose Acetate-Butyrate	Injection	.004	.0055	.0072	.005	.009
Cellulose Acetate	Injection	.0038	.0055	.0072	.005	.009

Of course it must be realized that the accuracy with which molded parts are produced will also depend upon the care observed in preparing the mold. Very close tolerances can be held if much of the finishing and alignment is left until after the steel has been hardened. This is more expensive, though under certain circumstances may be warranted. Dimensional tolerances for molded

plastic parts have been the subject of careful study, and values to be incorporated in the design must reflect the variables of molding technique as well as the dimensional stability of the material. S.P.I. has made an initial survey of molding dimensional tolerances and has classified them as follows: (1) Fine tolerances—very close limits possible through strict supervision; (2) standard tolerance—usual tolerance which can be held in production and (3) coarse tolerance—permitting considerable latitude in dimensions.

Shrinkage of molded plastic parts is a problem which confronts every designer at one time or another. While the designs should specify tolerances in keeping with probable mold shrinkage values, there are certain other factors involving shrinkage which are not easy to evaluate. Shrinkage from mold dimensions constitutes one type of shrinkage and usually can be estimated as a function of the material employed and the temperature and time of the molding operation. On the other hand, shrinkage of the molded parts in service depends upon the material employed, state of cure of the thermosetting plastics, temperature of application, vapor pressure of plasticizers in thermoplastic materials, humidity, etc.

The probability of these changes occurring should be anticipated and the designer should make adequate provisions for them, generally through the assignment of liberal tolerances, or at least in designing the piece so that operation will not be affected by the slight change that will occur.

Evolution of the Design

Many precautions are observed in the evolution of an engineering design in plastics from its initial conception to the time that parts are received from the production molds. Particular care must be exercised when large mold investments are involved, as may be the case for molded machine housings. Industrial designers have been active in promoting designs in molded plastics, and by working closely with engineering departments of the various manufacturers many commendable articles have been produced. From sketches and models submitted by the artist, accurate layouts are drawn by the draftsman, followed by detailed drawings.

While a clay, plaster-of-paris, or hardwood model finished in some enamel may serve to translate the conception of an artist to a tangible form, experience has shown that an accurately machined article is to be preferred before a mold is ordered. Consequently, when a preliminary design has been decided upon and detailed drawings completed, a model is accurately machined from metal or, preferably, from a solid piece of plastic material of the same color and finish as the proposed production model. Working tolerances and clearances often can be checked from this model. At this stage of the design, consultation with the custom molder may reveal certain features that would be costly to reproduce by molding. Worthwhile savings may be effected on his judgment and experience. It usually is advisable to finish the surface of the model inasmuch as objectionable highlights, sharp curvatures, or unbecoming flat areas will be revealed, and the necessary changes made.

Whenever possible, especially when large quantities and multiple-cavity molds are involved, a single cavity experimental mold will prove to be a wise investment. Failure to invest in an experimental mold or in an accurately machined model is the cause of expensive changes in production molds. The experimental mold serves many useful purposes:

1. Accurate estimates may be made for mold shrinkage and after-shrinkage in the plastic material, and thus allowances can be made in production molds
2. Appearance of the article as a molded piece may be far different from the model machined from wood or metal, thus necessitating further changes in the design
3. The manufacturer may wish to send a number of experimental models to prospective customers. Pieces from an experimental mold would be less costly than if each were machined individually. From the comments of the customers, the final design may be arrived at, and adjustments made in the production mold.

Often an experimental molding in a transparent or translucent material will reveal data on wall thicknesses of uneven surfaces or working clearances not suspected in a solid opaque model. When the final design has been approved or the experimental single-cavity mold noted as satisfactory, the multiple-cavity production molds may be ordered. Successful results are assured

only when proper precautions have been exercised in the evolution of the design. Never should a design go directly from the drawing board to the mold without building a model of reasonable accuracy.

Once the design has been accepted, through approval of an accurately machined model or, preferably, of a unit from the experimental mold, changes are costly and increasingly difficult to make the further into production the design progresses. If the designer is aware that some changes are inevitable, he should inform the molder, who may make provisions for accommodating these changes in the production mold at the least possible expense.

The design of molded plastic parts requires not only knowledge of good mechanical design principles, as have been outlined in this chapter, but also a good comprehension of the tools or molds to be used in turning out the work. When this background has been attained, the designer can really design in plastics.

Inspection and Preliminary Tests

Of major consequence to the success of any design in plastics is the inspection and preliminary tests given to the plastic parts prior to their inclusion in production assemblies. Tests upon the suitability of the materials employed should be conducted well in advance of the actual molding operations. They should be followed in turn by inspection of preliminary parts from the experimental molds or punched laminated parts. Finally, the first lot obtained from production molds should receive a last thorough inspection for mechanical suitability and adaptability to the remainder of the assembly. Briefly, inspection tests upon plastics parts constitute:

1. **Material Qualification Tests**—Electrical, chemical, or mechanical properties should be thoroughly tested under the severest conditions of the intended application. Any deviation or failure to comply with requirements is cause for rejection.
2. **Preliminary Qualification Tests of Finished Samples**—These tests are designed for parts furnished from the single cavity molds or temporary dies to check primarily mechanical properties and clearances, and electrical properties. Particular note should be made of the tolerances that have been ob-

served, especially on inserts. Molded pieces should be checked carefully for surface flaws and material imperfections and contours carefully inspected for conformance to final drawings.

3. **Final Acceptance Tests on First Production Samples**—First samples obtained from production molds and dies should be subjected to a thorough inspection in much the same manner as were the samples for preliminary qualification tests. A number of complete assemblies may be made and submitted to service tests as soon as possible, to ascertain shrinkage changes which may occur during operation.

The type of service to which a part is to be subjected and the kind of materials employed determine the nature and severity of tests. For example, material inspection methods for molded urea plastics or lightly colored cellulose plastics are somewhat more stringent with respect to appearance. As a result, a number of otherwise mechanically sound parts may be rejected because of material imperfections. Translucent and transparent materials are among those which have a high rejection rate, not only because of slight impurities, but also because of the presence of minute air bubbles difficult to free from the molding powders. Other properties requiring careful judgment on the part of the inspector are heat resistance of the plastic, shrinkage, and odor at the maximum service temperature. There is only one way to find out and that is to subject the plastic piece to the maximum temperature which it may be expected to encounter and keep it at that temperature for the maximum possible time which may be encountered in some abnormal operation. This test should be repeated a number of times until reasonable assurance is obtained that the material is satisfactory in relation to the remainder of the assembly.

If an odorless material is to be provided, a slight trace of an objectionable odor should prompt rejection. If the manufacturer cannot produce absolutely odorless preliminary samples, it is unlikely that he will fulfill the requirements in production. Placing the molded piece in boiling water for a few minutes, and then smelling the part will reveal the presence of a phenolic odor in thermosetting phenolic plastics.

For checking tolerances on molded cavities and contours there are miscellaneous inspection gages of value. Master templates, manufactured with precision tools and gages known to be

accurate are helpful in checking the unusually shaped curvatures sometimes found in molded parts. The shape of the mold may conform with the master template, but that is no criterion for the molded piece which may undergo a shrinkage tending to distort the external shape of the molded part. Corrections to the mold cavity then usually are made. For the inspection of openings in molded pieces and for the location of inserts, accurately built gages are helpful. These master gages must be kept in good condition and not mishandled for, through the entire production of the plastic parts, they will serve as a standard for the pieces that are turned out.

It is also good practice to check the molder's gages for accuracy and agreement to insure the rejection of inaccurately molded parts at the place of manufacture as early as possible. This will save much wasted effort on the assembly lines.

If parts require a final buffing operation, absolute cleanliness and freedom from finger prints and stains should be observed. With thorough preliminary inspections service problems will be minimized.

Chapter X

Inserts for Molded Plastics

In many respects the molding of plastic materials is in effect an assembly operation. From two to hundreds of individual components have been assembled by means of the molding operation into an accurately aligned, integral structure. During the molding process the plastic material not only captures all of the fine details impressed on the molding surfaces, but also unites other components, called inserts, into a strong permanent relationship to one another. Not all molded parts have inserts, though the experienced plastics designer knows well the advantages of inserts, and may at times specify a molded part primarily for its advantages in assembly.

Inserts in molded plastics have appeared in innumerable guises. Sometimes they introduce their own weaknesses, though more often their contribution to design efficiency outweighs the disadvantages. Types of inserts employed in molded plastics are listed in Table XLIX together with their functions.

TABLE XLIX

Functions of Inserts in Plastics

Type of Insert	Typical Function
Resin impregnated paper, canvas, or matted fiber	Localized reinforcement of molding compound, as about some hole
Male and female threaded parts (brass, aluminum or steel)	For attachment purposes, or as electrical binding posts
Small metal pins	Radio tube bases, plug connections
Metal stampings and eyelets	Electrical connections and assembly
Vulcanized fiber	Improve arc resistance
Glass viewing window	Molded trim about periphery of glass renders it more serviceable
Wood	Lightness in weight or to facilitate further cementing
Rubber	Rubber vulcanized simultaneously to secure resiliency

Application and proper design of inserts are major factors in designing plastics for production, not only simplifying assemblies but also strengthening the piece in some cases and decidedly enhancing the design possibilities of the molded parts. In assembling miscellaneous articles, engineers usually favor the minimum

of handling of small parts and the elimination of small, loose pieces as far as feasible. A threaded insert not only means one less screw-machine part to handle in the assembly, but its correct positioning with respect to the other by the molding operation. Other inserts, such as fiber or metal rings, improve tolerances on the molded part, when designed in the proper manner. For the most part, inserts are not affected chemically by the molding material, either during the resin flow of the molding operations or by the thermosetting materials after operations. Special precautions sometimes are necessary to protect thio-urea molding compounds from steel inserts by chromium plating the parts. Nevertheless, inserts are widely employed in plastic design and their use should be encouraged.

Inserts most commonly employed in engineering designs are metal parts turned from hexagon or rod stock in automatic screw machines. These threaded inserts locate molded members with respect to the remainder of the assembly. Their external shapes are undercut to avoid turning or pulling out of the molded piece. Two comparatively simple methods may be followed for providing anchorage for the insert within the molded part during the molding operation:

1. Turning hexagon or square stock with an undercut. Molding material will fill the undercut completely, and prevent it from pulling out
2. Turning round stock with a deep diamond knurl. At least 0.010-inch deep is good practice. Avoid sharp edges on the insert.

After machining, the inserts may be plated to improve appearances. Nickel and chromium plating are not affected by molding materials. It is also feasible to design small machined metal inserts without weakening the molded section in which they are placed by gradually tapering off the end of the metal insert into a small rounded, cone-shaped apex. A flat area has practically no resistance to shearing stresses and, if tapered in the proper manner, the metal insert will act as a reinforcement down to the tip of the cone apex. This practice may be better understood by referring to *Fig.* 79.

When inserts are used for attachment of molded parts to another assembly, they should be designed so that the clamp-

ing force is not withstood by the plastic material. The plastic may creep under stress in the course of time and the assembly loosen. For that reason, the design should cause the clamping stress to be withstood by metal rather than by plastic.

Other considerations should be given to the design of small metal inserts for production. Many inserts are threaded internally

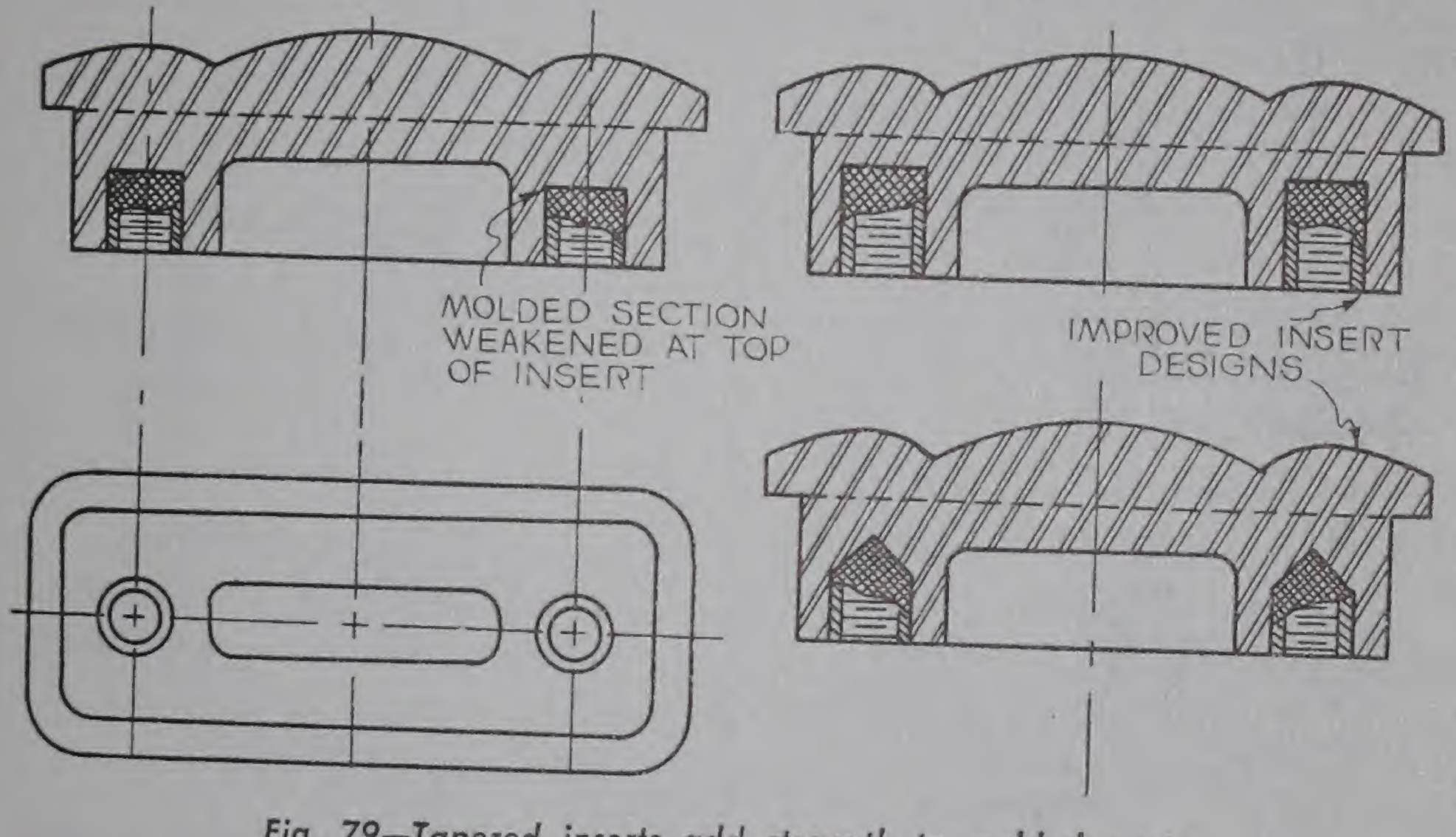


Fig. 79—Tapered inserts add strength to molded part

or have protruding male threads, which must be kept free of molding compounds. Design standards for inserts have been established by the S.P.I. and are now in general use by the plastics industry. Good practices for inserts with internal and external threads, *Fig.* 80, *a* and *b*, follow:

Internal Threads:

1. Terminate knurl about 1/64-inch from the surface that is to be flush with surface of molded piece. This will permit a snug fit and avoid inception of compound into threads, which would occur if the knurl ran to the end and turned up a burr
2. Leave round shoulder on end of insert for positioning in mold cavity and provide a seal against the compound
3. Run a reamer through tapped threads to remove burrs, and thus allow for easy attachment of insert to holding pin in the mold
4. Mold insert with drilled hole and tap the insert after molding it in place.

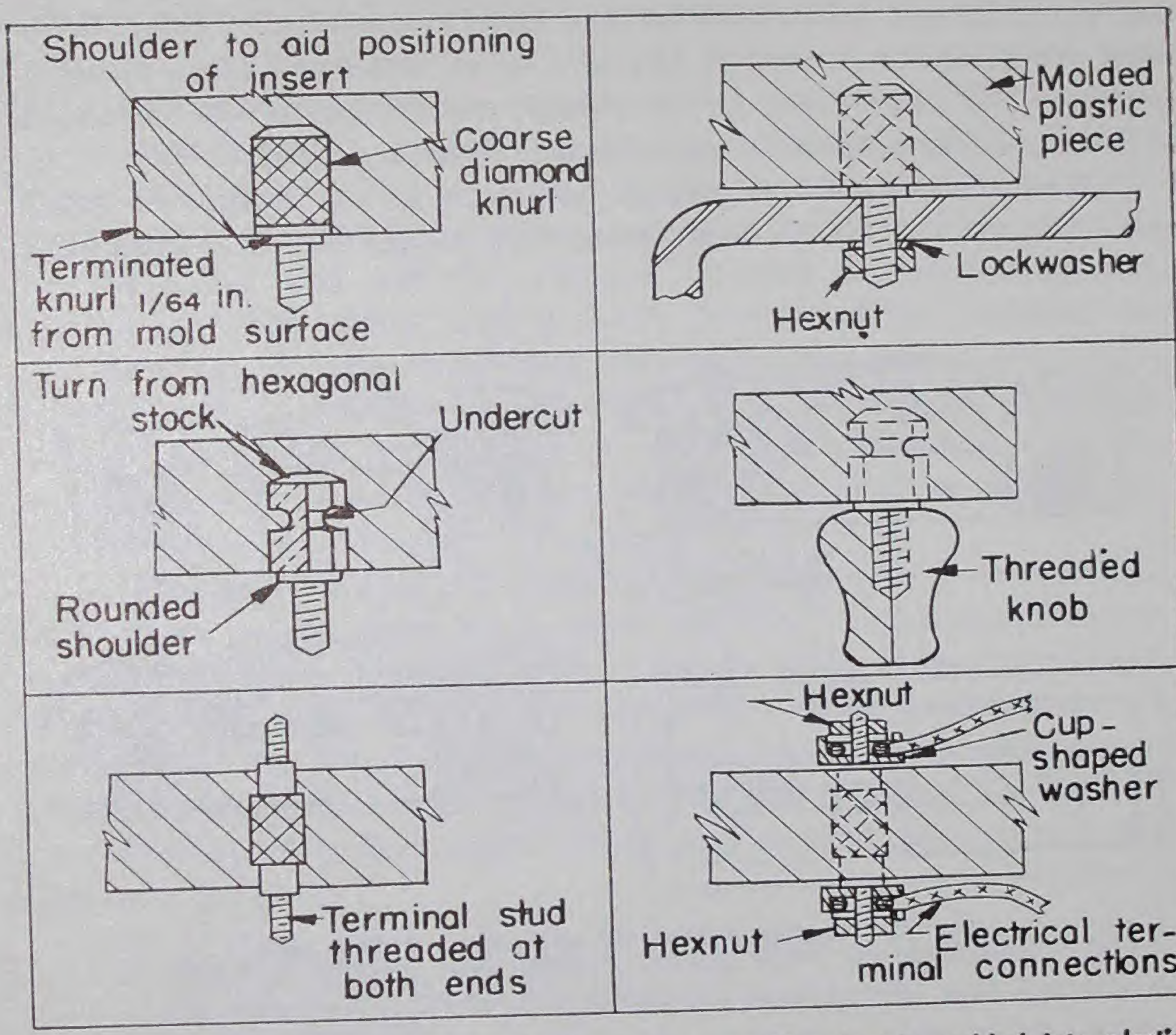


Fig. 80a—Representative assemblies involving screw-machine inserts molded into plastics

External Threads:

1. Design smooth shoulder on threaded member for positioning in mold cavity, providing a seal against molding compound which tends to run down the threads
2. Terminate the knurl about 1/64-inch from the edge of the molded surface to avoid burrs that prevent a snug fit.

By the preceding expedients, cleaning costs and retapping of inserts will be avoided and production speeded up. Proper precautions must be observed for plastics have sufficient flow during molding to enter threads in inserts. Inserts should be freed of oil and chips by careful washing and cleaning procedures. This is particularly important when a perfectly air tight seal about the insert is to be maintained.

Design of metal inserts is comparatively simple and entails

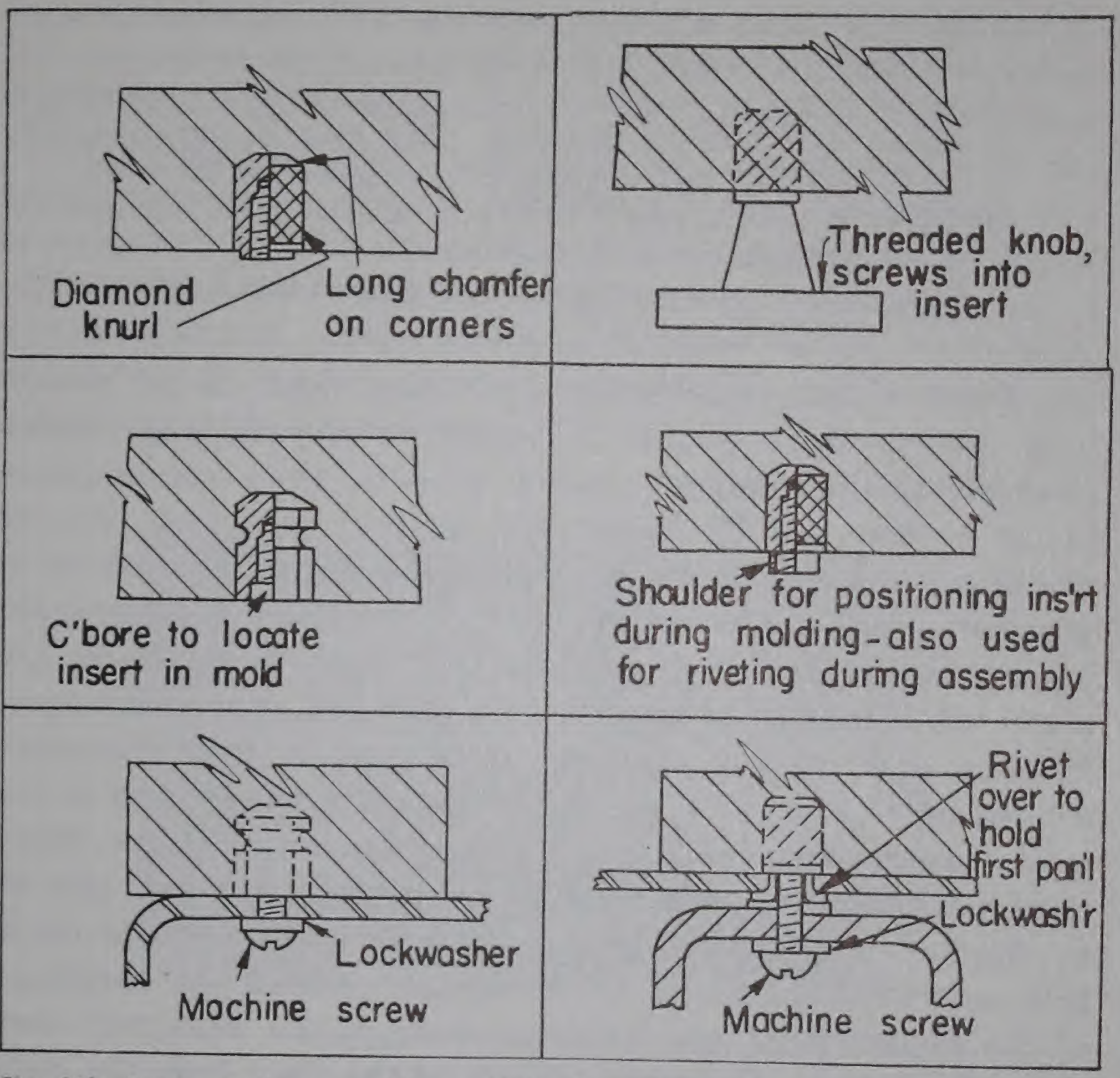


Fig. 80b—Representative assemblies, additional to those shown in Fig. 80a, of screw-machine parts molded into plastics

no unusual production difficulties. For the main part small metal inserts turned from brass stock answer most purposes. The manufacturer sometimes provides the custom molder with inserts turned from his own automatic screw machines, an economy often observed, inasmuch as the custom molder may not be as efficiently tooled up for production work of this nature. When large quantities are involved, transportation charges from manufacturer to molder are reduced per unit piece, and do not add appreciably to the cost of the final product. Whether the molder or manufacturer machines the inserts, the manufacturer prepares the drawings for the pieces so that there will be no misunderstanding about the parts that are to be attached thereto.

Attachment of Inserts: Four general methods of attaching small metal inserts to molded parts are as follows:

1. Piece is placed in molded preforms. The preform is the molding material cold-pressed to the shape of the cavity
2. Insert is positioned in the mold cavity, preferably parallel to direction of molding pressure. This may be done manually or by special insert locating fixtures placed in the press
3. Insert is pressed into a molded hole after piece has been removed from the mold and is still hot
4. Molded piece is drilled and insert pressed into position.

The first two methods are used most widely in the attachment of inserts to molded parts, the actual anchorage taking place during the molding operation when the resin has an opportunity to flow and fill knurls and external undercuts. Inserts are added manually to the mold after the cavities are cleaned in preparation for the next operation. If the insert is to protrude beyond the molded piece into the mold itself round pieces are preferred, as machining operations for a hexagonal or square opening in a mold for an insert are more involved than a straight drilling operation for a circular piece. Additional sections to the mold sometimes are required for holding noncircular pieces. There is an advantage to the locating of small inserts by mold pins or by the insert body itself, in that the spacing between inserts is held accurately in the mold. As already pointed out, shrinkage of the molded piece upon cooling outside of the mold may alter these dimensions. However, removal of the piece from the mold and placing it upon slightly tapered sizing studs, will insure greater accuracy in dimensions.

Horizontal inserts offer special problems to the molding operations. When used in direct compression molding they are subject to distortion in the mold cavity or their supporting pins experience severe shearing forces due to the pronounced pressure gradient upon the molding material, when the force enters the mold cavity. These problems are not so serious in transfer molding where the material is forced into a cavity already closed, and simple locating plates and pins may be used to support horizontal or oblique inserts. Generally, these molds are of the split cavity type. Transfer molds are well suited to handling complicated inserts such as those shown in *Fig.* 81

Symmetrically shaped inserts, when placed so that their major axes are parallel to the direction of pressure gradient will not give much difficulty in compression molding. When inserts are

located at the top of the molded piece, they may be attached to the descending force or plunger pin. This is also a convenient way of attaching thread forming rings in compression mold design.

A striking example of a group of multiple inserts is the molded commutator illustrated in *Fig.* 82. Commutator bars may be supported individually or a continuous copper ring may be molded into position, and the slots cut into position in a separate milling operation after molding. Transfer molds are readily adapted to the molding of small commutators as they will cause a minimum of distortion upon inserts.

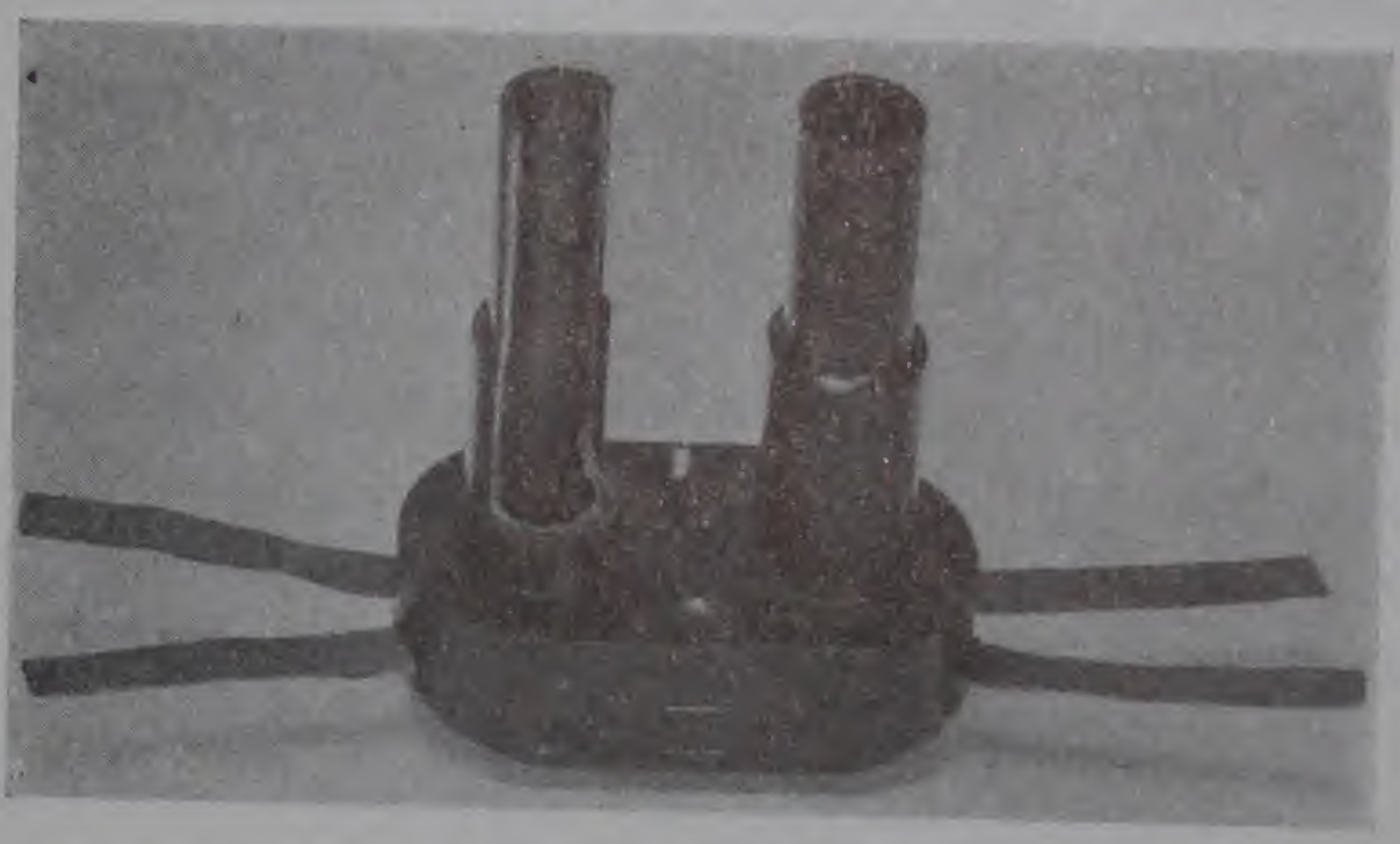


Fig. 81—Copper strips and fiber inserts are utilized in this transfer-molded piece

The use of injection molds or transfer molds is valuable particularly in molding about large or complicated inserts. Thermoplastic materials have met with particular success, most notable is 18 ounces of cellulose plastic about a steel core for an automobile steering wheel—on a production basis. Wood, metal, and glass members similarly have comprised the bulk of inserts for injection molding. The bezel of cellulose plastic molded about glass plates has involved an unusual and difficult technique, though they now are being successfully molded. In some injection molds rubber vacuum cups can be used to hold glass inserts in position. Injection and transfer methods have proved more satisfactory for unusual inserts.

Long slender core pins should be avoided, inasmuch as pressures developed during compression molding tend to distort these pins appreciably if their length is twice the diameter or more.

Fig. 82—Cross section of molded commutator

Pins also are broken during the closing of the mold, where pressure gradients over small areas may be high. This applies not only to core pins but also to inserts which, if supported at one end, should be as short as is practical. Conditions are more favorable for inserts during injection molding, where the pressure builds up more uniformly with the smoother flowing thermoplastic material. Too short an insert is not always desirable either, inasmuch as there is too little molding material to hold square or hexagon stock if they terminate near the wall of the molded piece. Against the case for inserts molded into place during the molding operation may be cited:

1. Probable increase in the molding time cycle, because of the extra handling of parts and positioning of inserts in the mold
2. Possible chasing of threads filled with molding compound
3. Difficulty of maintaining exact tolerances between inserts.

The final alternative for attaching parts to the molded pieces is to mold undersize holes by core pins and use self-tapping screws, or mold through-holes and use rivets, eyelets, or through-screws for assembly purposes. In radio bases, the ends of the prongs may be conveniently riveted over after insertion in molded or laminated pieces as shown in *Fig.* 83. A center guiding and polarizing pin usually is molded integral with the base. Care must be exercised in riveting so as not to crack the molded piece. When many riveting operations are required, an impact-resisting

plastic such as fabric-filled or cord-filled phenolic, or cellulose derivative may be specified.

Plastics may be drilled and tapped, though in production such operations require high-speed tool steels or carbide tipped tools, as the tools get quite hot. The drilling and tapping of molded plastics may be necessary when a molder has a limited produc-

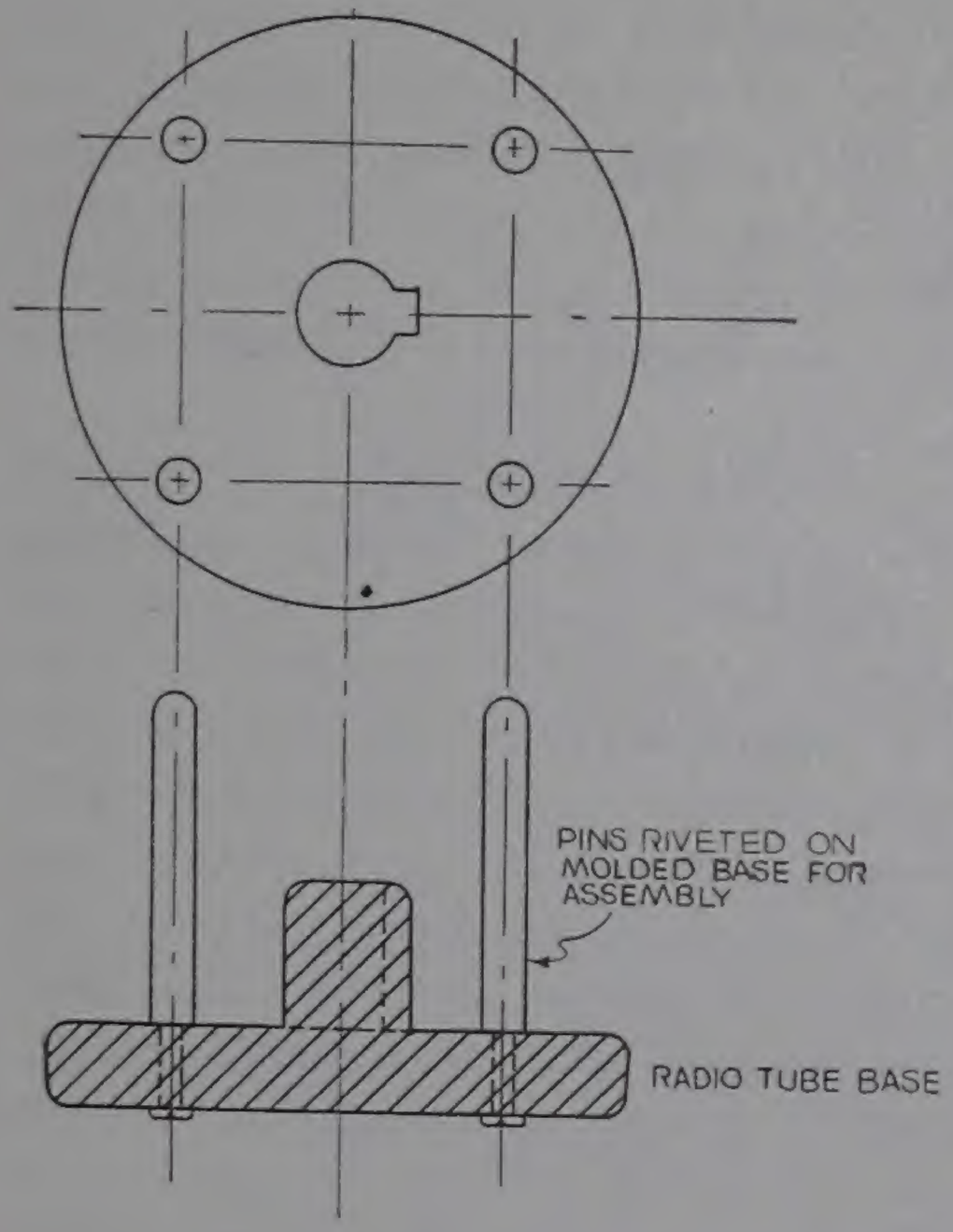


Fig. 83—Radio tube base, showing attachment of pins

tion or does not wish to go to the expense of making the mold more complicated to introduce the coring pin or threaded stud. Holes may also be drilled in the plastic if there are critical tolerances to be maintained between centers—tolerances smaller than those normally permitted in the design of molded parts. In fact. it would be a better practice to after-shrink the molded parts by baking, and then perform the drilling operation.

While the inclusion of inserts in the mold is almost the universal practice for compression, transfer, and injection molding, with cold-molding processes which shape the plastic through pressure alone, attachment or pressing in of inserts after molding is the desirable procedure. Parts are cured afterward by a separate baking in an oven. In the manufacture of kitchen cutlery, the metal parts are pressed into drilled rods of cast phenolics heated in boiling water. In this way, strong, satisfactory assemblies have been produced. However, the liquid resins may also

be cast about the metal inserts, if the latter have been given a lacquer coating to protect the plastic against contamination or guard them against the effect of any catalyst.

Molding Considerations: A number of practical design suggestions, useful in molding about inserts, particularly screw-machine parts, are offered herewith:

1. CLEANLINESS OF INSERT: All inserts should be thoroughly cleaned of any dirt or grease before assembling them in the mold. Under some circumstances sand-blasting may be justified on the knurled portion to insure adequate seal and bond of the plastic to the metal, particularly if the insert establishes a connection between an air-tight or pressure chamber and the atmosphere.
2. WALL THICKNESS ABOUT INSERT: Thickness of plastic about a metal insert depends upon many factors, including the thermal properties of the two materials, as well as the physical properties. A plastic with a low modulus of elasticity may, for example, be more satisfactory than a stiff, high-modulus material, even though the former may differ more appreciably in thermal expansion coefficients. The ability to creep and cold flow may alleviate some of the stresses which would otherwise develop between the plastic and the metal. Representative wall thicknesses recommended by the S.P.I. in their design standards for inserts, are shown in Table L.
3. FLOATING OF INSERT: In compression molding primarily, the tendency for inserts to float or lift from the insert holding pins may be quite pronounced. This may be controlled by several methods, which include the use of tapered insert holding pins (about 0.003-inch per inch taper is sufficient if the thread dimensions are up to size); split pins or spring tension pins are practical upon blind hole inserts; an extended shoulder which engages in the face of the mold; or a smaller

TABLE L

SPI Recommendations for Material Minimum Wall Thicknesses Around Plain Round Inserts (inches)

Material	1/8-in. diam Insert	1/4-in. diam Insert	1/2-in. diam Insert	1 in. diam Insert
General-purpose phenolic	3/32	5/32	7/32	11/32
High-impact phenolic	1/16	1/8	3/16	9/32
Cellulose acetate	1/8	1/4	1/2	1
Mineral-filled melamine	3/32	5/32	7/32	11/32
Polystyrene	3/16	3/8	3/4	1 1/2
Polyethylene	1/16	3/32	5/32	7/32
Polymethyl methacrylate	3/32	1/8	1/4	1/2

diameter locating pin to back up the rear of the insert and keep it in place (this will necessitate a hole through the plastic). In transfer molding, the tendency to float is less pronounced, particularly when the mold exerts a squeezing action upon the insert before the material is transferred into the cavity.

4. THERMAL EXPANSION: Plastics have higher coefficients of expansion than most metal inserts, a factor which becomes more important as the size of the insert grows. Aluminum alloys have expansion coefficients nearest to the thermosetting plastics.

Unequal thermal expansive coefficients may cause stresses in the molded materials, which would limit their usefulness. Further, after-shrinkage of the plastic while in service may lead to further complications.

Molded phenolics are better in that respect, inasmuch as their coefficients more closely approach those for the metals. Large metal pieces have been molded inside of plastic parts with a preliminary coating of rubber, which tends to compensate for the difference in thermal coefficients of the metal and plastics. This procedure has been found satisfactory for large copper bus bar contacts molded into position. When the metal pieces attain sizable proportions as compared to the plastic present, it may be necessary to preheat them prior to placing them in the mold to avoid sudden chilling action.

5. THREADS FREE OF MOLDING COMPOUNDS: By exercising the proper design precautions threaded inserts may be kept free of molding compound. When female threads are employed the molding composition will not enter, as long as the end of the insert that appears on the surface of the molded parts is flat and free of burrs, so that the bottom of the mold will form a good seal. On the other hand, male-threaded parts should protrude slightly, with a small shoulder seating in the mold cavity. Otherwise, if flush with the surface of the mold, the molding composition may run down the threads during molding. Removal of molding material from threads slows up operations and must be avoided. Otherwise, it will be necessary to chase the threaded inserts after molding.

Miscellaneous Inserts: Among miscellaneous inserts, other than metals, which broaden engineering design possibilities, are fiber, glass and semicured molding board or laminated plastics. The significance of the latter is apparent insofar as strengthening the molded piece is concerned. Fiber has been of value in locations where the molded piece is subject to arcing, minimizing

the possibility of burning phenolic plastic composition, which is subject to carbonization and disintegration. Fiber inserts often will give good insulation and arc resistance to metal members, such as terminal contact points.

Plastic bezels, of various sizes, have been injection molded about glass bases which are used as inserts. The bezels on shrinkage and cooling make a tight joint and simplify the problem of providing a smooth finish on the edge of the glass. An enterprising manufacturer has been experimenting with the idea of actually molding in "sealed-in" compact condensers into the housings of the small portable electric appliances. The purpose of the condenser is to reduce radio-frequency disturbances emanating from the motor. Similar ingenious designs have appeared. It is a significant fact that the suggestions of molding about condensers, glass and die castings have originated largely from design engineers, who have visualized the possibilities of plastics in their designs.

Combined Metal and Molded Parts

There are designs of metals and plastics in which the size and volume of metal inserts are comparable to the amount of molding material present. Much study is given to these combinations to bring out the best qualities of both materials. Phenolics molded by transfer molding methods and cellulose plastics molded by injection molding machines have been noteworthy in these applications. Among the many design advantages accruing from combinations of this nature are:

1. Economy in the use of the plastic material means a saving in the cost of part
2. Metal receives a heavy insulating coating molded directly at those locations where it is most needed
3. Corrosion resisting surfaces are applied to the metal article
4. Structural reinforcement of the plastic is made possible by the metal member.

Plastic materials are comparatively costly when compared on a pound basis with metal or wooden articles. For this reason sheet metal stampings, die-castings and wooden cores have been used to supplant heavy sections of molding material. Wooden

cores require special preparation in that they must be thoroughly dried and contain no moisture. For the greater part, the application of plastic materials over wooden or metal cores is conducted by injection molding operations, and generally with thermoplastic materials. Considerable attention continues to be given to the development of molding cellulose plastics over metal cores, for automobile handles. The advantages from a strength, appearance, and durability standpoint are obvious.

The trend toward the use of die-castings, particularly zinc castings about which are molded various plastics is pronounced. Refrigerator handles, temperature-control knobs, and bezels of recent designs have been injection molded to a depth of 1/16 to 1/8-inch. Not only is an attractive appearing design produced, available in many colors, but a piece more pleasant to the touch of the hand also results. Die castings and plastics have a large field of application in the automotive industry. Automobile door handles are but one example where a saving in numerous operations has been effected through the use of molded plastics. Injection molding transforms a rough casting to a finished article, whereas in the past, as many as a dozen steps were required to bring the handle to final form. Similar applications are possible with other automotive parts. Another significant example of die-castings and molded parts is an electrical cutout used on a single-phase motor to cut out starting resistances as the motor comes up to speed. The die-casting and a molded part are designed as one unit. Insulation protection and simplicity are the keynotes of this design. Small portable motor-driven tools use molded plastics in their drive mechanisms for insulating the driven head parts from the armature shaft. This is an excellent safe-guard, particularly if the driven part touches the human body as in case of hair clipping machines.

Examples of large metal inserts in molded parts for engineering designs are numerous. Many mechanical advantages accrue from this practice, particularly as shown in *Fig.* 84 by the die-casting, about which is molded phenolic plastics. The U-shaped piece is used as a drawer pull. The smoothness and comfortable feel of the plastic is augmented mechanically by the large metal core. Another example is a connection for a beer pump line. Molded in a transfer mold, two large pipe plug members and two electrical terminals are joined into a composite unit.

In some molded parts there may be more metal than there is plastic. No better example exists than a shielded spark plug, in which a protective coating for the ignition cable is molded directly into the shielding encasement from two directions. This unit likewise was produced in an injection or transfer type of mold. Precautions must be taken to secure the metal members with respect to the molded plastic. Knurls, undercut surfaces, and holes often are used to advantage for this procedure.

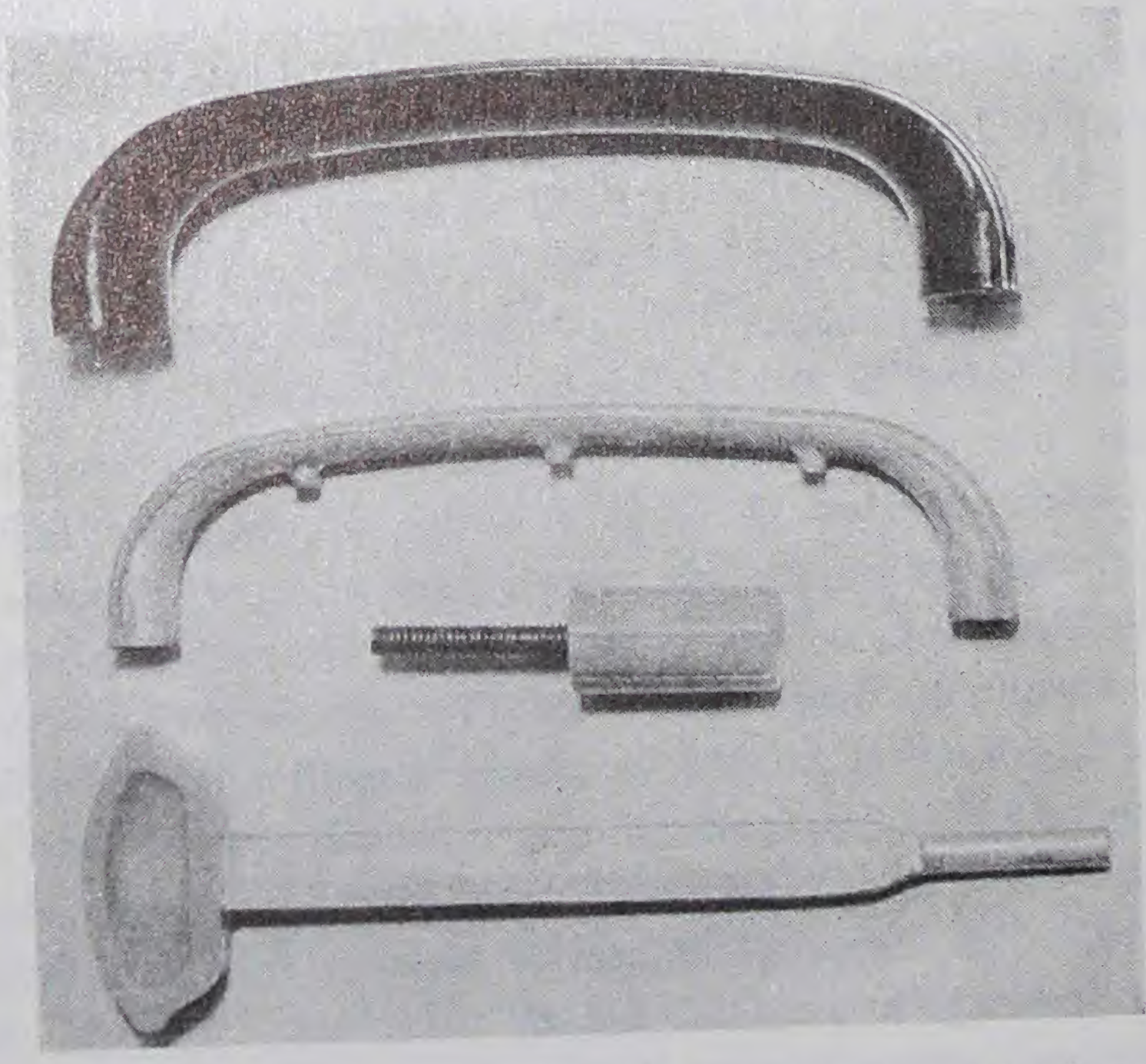


Fig. 84—U-shaped drawer pull with die-cast insert molded handle; and (lower view) metal inlay molded in handle

Among other units wherein molded plastics have supplemented the design features of metal pieces are the handles for small hand tools. Injection molded cellulose plastics bind the tool tightly and give an attractive handle with a sturdy, durable grip. A large quantity of handles are similarly produced in one injection operation. In similar assemblies, cellulose derivatives have been cemented on as handles for drills, chisels, files, and a wide assortment of small hand tools. These have proved much more popular than the wood they replaced, not splitting and offering a comfortable grip to the user. Not only have plastics proved outstanding as handles for hand tools, *Fig.* 85, they have even

Fig. 85—Plastic handle of this saw has smooth surface, low heat conductivity and, being tough, will withstand rough treatment

furnished the tool itself, as for example in the manufacture of hammer heads. Hammer heads of plasticized polyvinyl acetal have proved quite useful for many operations where quietness and non-sparking qualities were desired, and severe denting of sheet metal was to be avoided.

In the field of plumbing fixtures, plastic and metal combinations have been outstanding, the most efficient design generally resulting from a combination of the two basic materials. For example, attractive, colorful plastic handles for faucets will capture the public fancy, offering the functional advantages of freedom from tarnishing, comfort to the touch in spite of hot water, and adaptation to color schemes prevailing in the modern bath-

room and kitchen. On the other hand, considerable torque and twisting of the valve stem may occur during the life of the unit, in which case a metal body may be preferred for its mechanical durability. Inside of the valve, a laminated plastic with a rubber facing will provide a seal-off washer superior to the leather or whole rubber types now used. The pipe threads at the end of the valve could be in plastic, but most plumbers would probably show a preference for a metal fitting on which they could 'lean heavily' at the time of installation.

During the Second World War, the shortages of brass and bronze led to the adoption of floats and fittings of plastics in the construction of toilet flushing facilities. From all indications, these have proved highly satisfactory in eliminating noise and corrosion. Toilet seats of wood faced with thin sheets of thermoplastic, or seats molded entirely of plastic have been produced in large quantities.

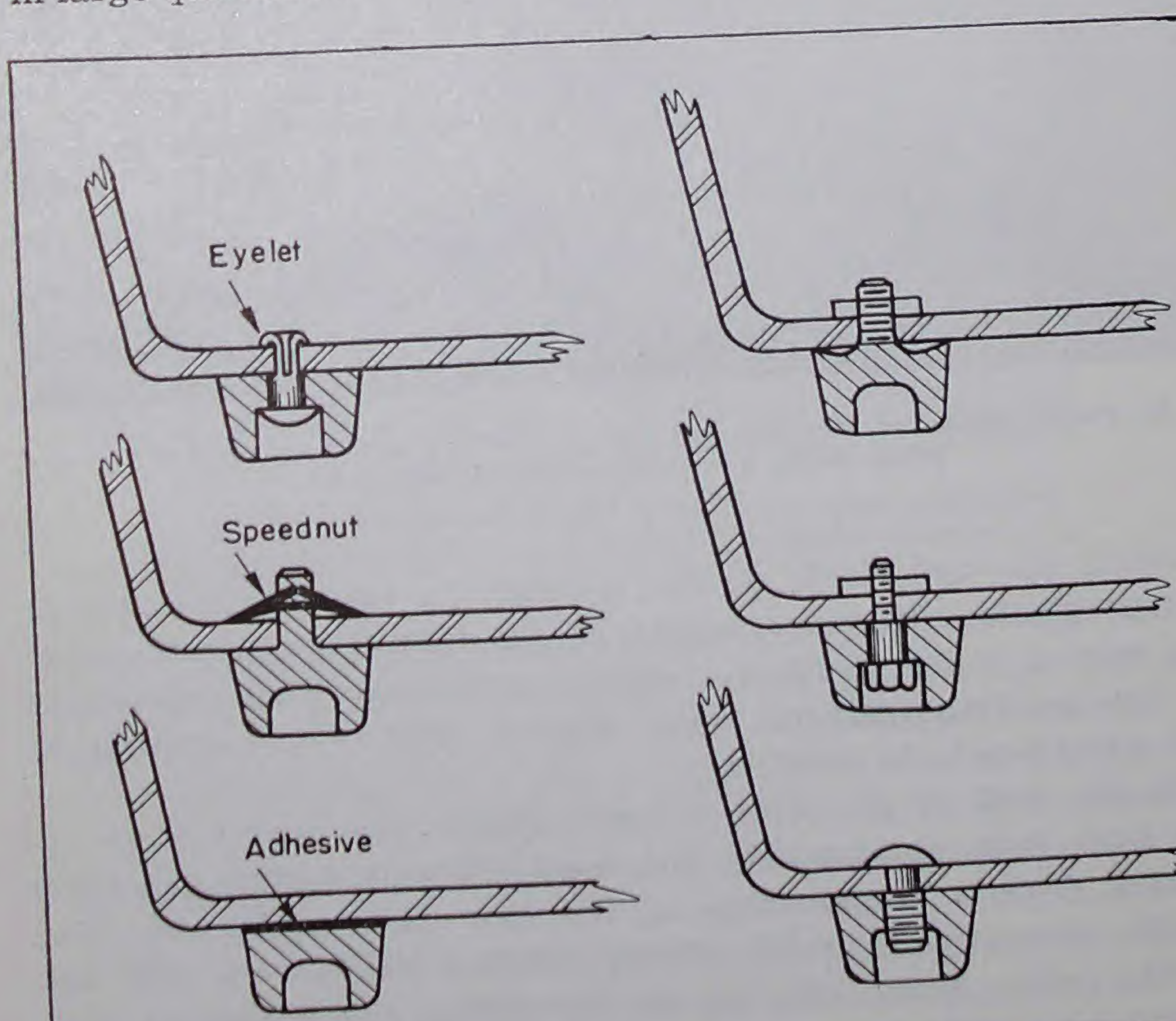


Fig. 86—Some methods of attaching plastic feet to metal stampings

Considerable interest has been focused upon conduits and pipes of plastics, as well as junction boxes for the attachment of the conduit. Compared to metal they are at a disadvantage at the time of assembly with heavy pipe wrenches, though smaller units may be readily sealed or heat welded together. From the standpoint of corrosion resistance, they offer good service. Their low thermal conductivity would mean less tendency to freeze in cold weather. However, they would suffer more in hot weather or in the presence of hot fluids. While thirsty rodents will attack pipes of all description in which water has been flowing, they would more readily chew through a plastic than metal pipe. In electrical conduit, the plastic pipe would have to be of a non-burning variety such as polyvinylidene chloride ("Saran").

At present, plastic pipes and conduits appear best suited under the following conditions:

1. Unusual cross-sections other than simple round shapes
2. Handling of highly corrosive acids or alkalies (acid-resisting phenolics)
3. Flexible conduit for handling wide variety of organic chemicals (polyvinylidene chloride, polyvinyl chloride and polyvinyl alcohol, for example)
4. Airtight connections such as are provided by heat sealing.
5. Permanent flexibility—particularly under outdoor conditions.

In the preparation of numerous instruments, machines, and household articles, it generally is necessary to provide means of attaching plastic molded feet on a metal stamping or panel. Because this problem is representative of so many other equivalent machine design problems, some additional methods of assembly are noted in *Fig.* 86. With the development of practical, high-strength plastic-to-metal adhesives, this method of fastening should also be considered when the projection of a rivet head or screw may be objectionable.

Thermal Expansion Considerations

Differences in the heat conductivity of metals and plastics and differences in the thermal expansion coefficients are the basic problems which the designer must consider in every combination of plastic with metal. The essence of these problems

were discussed in the chapter on the thermal properties of plastics, where the expansion coefficients and heat conductivity ratings were compared. It was also pointed out that while the average plastic expands 2 to 5 times as much as the average metal, stress failures are more apt to occur due to the much higher heating rate of the metal, which always is the first to reach a high temperature or the first to cool.

Nevertheless when heating or cooling do not take place too rapidly, it is possible to match the expansion and contraction of metals and plastics. Aluminum alloys are available with the same expansion coefficients as plastics (phenolics), and stresses due to thermal differences may be held to a minimum. In the manufacture of plastic templates which are pressed on flat engraved metal plates, the author has found that greater accuracy may be maintained when aluminum alloy sheet, rather than brass sheet, is engraved and heated simultaneously with the plastic. The plastic sheet pressed into the aluminum alloy sheet will hold dimensions more accurately. This problem is quite important in the manufacture of precision scales and protractors, and the tools for them.

In designing metal and plastic combinations there are several design procedures which may be followed to advantage:

1. Design as large a heat-radiating surface as possible on the metal insert in order to reduce its temperature and the amount of heat it will transmit
2. Apply a thin coat of rubber or its equivalent upon the outside of the metal insert
3. If the metal insert is a long, continuous strip and is to be bonded to the plastic along its entire length, divide at frequent intervals, say every inch, or introduce expansion joints at frequent intervals
4. Introduce about the insert at the time of molding, a preform of asbestos-filled phenolic which not only will take higher temperatures, but which will conduct heat more readily and reduce the temperature gradient at the metal insert edge
5. If the metal component is a long continuous strip not bonded continuously to the plastic, employ oversize attachment holes, calculated on the basis of the relative expansion between the metal and the plastic
6. Allow ample wall thickness about the insert and reinforce with ribs. The ribs not only stiffen the part, but insure absence of flow or weld marks which would weaken the plastics considerably.

Inlays

Metal inlays on plastics have wide decorative appeal, augmenting the appearance of plastic parts. Particularly attractive are lightly colored inlays placed in dark backgrounds. During molding the resin flows and forms a thin, continuous film over the inlay, or adjusts itself so that the inlay and the surface of the molded plastic piece are on the same plane with no line of demarcation. Outside of the mere decorative applications, some manufacturers have found molded inlays an aid to identifying symbols on their products. The use of "Hot" and "Cold" inlay stampings on molded faucet handles has been suggested, inasmuch as the same mold could be used for both handles requiring only the change of inlays. Decorative buttons and knobs with molded initials of metal inlays, have been manufactured on a large scale with success, as have been dresserware, ash trays, advertising panels, and clock cases. One attractive piece molded with a metal inlay for use in a refrigerator is shown in *Fig.* 87. The metal inlay shown

Fig. 87—An unusual example of metal inlays on plastics

is a thin sheet metal stamping. While an extra die cost is entailed for punching out the design detail, the improved, durable pattern will always be readily identified.

Special methods for holding the metal inlays during molding operations are essential. Stampings are subject to displace-

ment from their original positions, causing a high rate of rejects. Small, short pins placed in the bottom of the mold cavity may be used to engage small holes in the decorative motif of the metal inlays, for protection against displacement. When a group of letters is required as in some tradename or advertising expression, the phrase may be punched out in a single stamping with connections between letters and held in position by two or three locating pins rather than a single pin for each letter.

To insure anchorage of the metal inlay stamping to the molded piece, it is good practice to face the burr side of the stamping in toward the molded part. This will give the resin binder a better gripping surface and avoid unnecessary displacement. Sand blasting the underside or turning down small lugs into the molded piece also may serve to secure the inlay.

When inlays are applied to large surfaces where there may be bending stresses, there is a possibility of cracking the thin resin film over the metal inlay. Such difficulties are not easy to overcome; the solution lies in strengthening the part by internal ribs to minimize bending. Another condition that may destroy the resin film over the inlay is heavy buffing of the molded part. It is good practice, however, to avoid placing the inlay across a mold parting line, where extra buffing usually is necessary on the finished part. When the design will permit the inlay to rise 1/64-inch or more from the surface of the molded piece, the question of inlays and their correct location within the molded piece is greatly simplified. The mold then may be grooved slightly to hold the inlay in place, turning out pieces satisfactorily on a production basis.

Another process for the attachment of metal inlay in plastics which has become popular is the "Chilton process." Grooves are molded into the surface of the plastic material or else cut into place by a pantograph machine. Flat metal stampings corresponding in every detail to these grooves are put into position in a manner illustrated in *Fig.* 88. First a hard base material is introduced into the groove. This is followed by the outside metal stamping which is slightly concave on the inside. When pressed down into place, the base material causes the outside stamping to dovetail out and imbed itself firmly in the side of the groove. A secure attachment is attained in this manner, though care must be exercised with the more brittle thermosetting plastics to avoid

chipping or cracking of the edges. Handles and control levers of various description are prepared in this manner. As the Chilton process is protected by patents, various molders have been licensed to do the work. On a production basis, the costs for stamping out inlays and pressing them in place vary from one to several cents apiece.

Other methods may be specified for the production of metal inlays. They have been applied to cast phenolic plastics, under the application of heat and pressure, the inlay imbedding itself

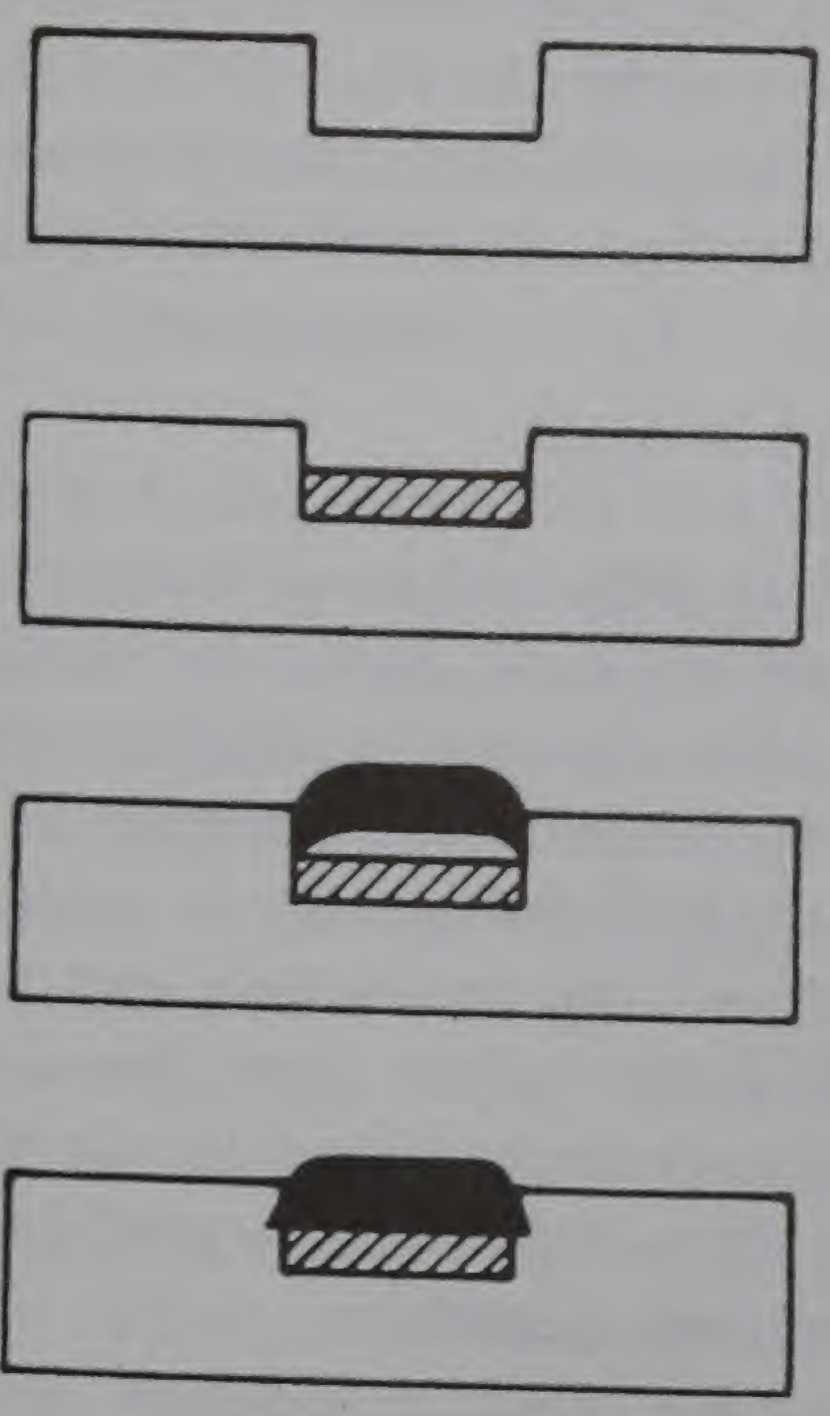


Fig. 88—(top to bottom) Chilton method for attaching metal inlays in plastics

a short distance in the resin leaving a continuous surface of resin and metal flush together. Laminated phenolic plastics have had inlays put into place in a similar manner, with the exception that the laminated material was not fully cured before final pressing. Thin translucent or transparent sheets of cellulosic materials also have been used to laminate metal strips to cellulose plastic bases, the thin transparent sheet being pressed directly over the inlay.

Among other molded designs that have lent themselves easily to metal inlays are cylindrical, chromium-plated bands on rounded shapes, where the ring may fit easly into position in the mold cavity without danger of displacement. Attractive effects also

have been obtained on molded cellulose plastic fountain pen barrels with metal inlaid by the Chilton process.

Branding cellulose plastics, cast phenolics, and thermosetting materials, is a widely used method for applying a trademark or decoration on the surface. As the name indicates, the operation is one of hot pressing or embossing. The article to be marked is placed in a fixture and pressed against a hot die sometimes made of hard brass to increase the heat transfer. The trademark or decoration may be filled with lacquer of a contrasting color from the molded piece. Colored foils may be embedded in much the same manner, a kick or hand press facilitating the operations which force the foil into a space formed by the die. A trademark or brand that is added outside of the mold often is a convenient plan, particularly where several markings are involved, requiring only different branding dies for each. Higher temperatures are an aid to branding phenolic plastics.

Roll-leaf embossing of phenolic and cellulose acetate plastics is common in marking molded plastics with designs or instructions. A typical cylinder molded for a light exposure meter, for example, has about 100 figures about a ¾-inch diameter periphery neatly rolled in and filled. In another production piece utilizing letters about a small molded knob, the roll-leaf embossing, in replacing the split cavity formerly used, reduced the production cost for a piece by more than one-half. All parts do not lend themselves to these methods, but designers should be prepared to use them for lowering mold and unit costs. This technique is particularly adapted to flat surfaces and thermoplastic materials.

The effect of metal coatings upon plastics depends on the thickness of the deposited metal. Heat resistance and resistance to vapors are improved appreciably. The metal plated articles not only have a wide decorative appeal, they also fulfill special engineering requirements where a conductive surface upon the plastic appears desirable. Various automotive and electronic hardware have made extensive use of metal platings on plastics. In the development of experimental injection molds of plastics, the author has found that a well-deposited electroplated metal coating over the plastic is an asset toward dissipating the heat of the molding operation. Adhesion of thick metal coatings is aided sometimes by a previous roughening of the plastic surface, as through sand blasting, followed by thorough cleaning.

Metal Plating

Metal plating on plastics has been conducted with a high degree of success. One outstanding application has been the honorable discharge pins of service men, which have been molded of plastics and electroplated over with gold. The electroplating of plastics involves the fundamental problems of rendering the surface of the plastic conductive to the passage of electricity. One method is to apply a stannous chloride solution, followed by a deposition of a thin continuous silver film, conducive to further plating operations. Another technique involves a conductive colloidal graphite coating, which is followed by electroplating. Metal powders burnished on the surface have also worked successfully as conductive coatings.

Self-Tapping Screws

Plastics are not always molded with metal inserts. For many designs, other means must be provided to facilitate assembly. Hardened self-tapping screws have been one answer to this problem. In some applications they have been proposed as substitutes for brass screw-machine inserts. Self-tapping screws form internal threads as they cut through proper-sized holes in the plastic material. Core pins in the mold provide holes of proper diameter for a given screw. Firm contact of the threaded members is obtained, giving adequate holding power and good resistance to vibration which might tend to loosen the screw. The self-tapping scraws are removable, and capable of reassembly without appreciable loss of the security of attachment. Small self-locking nuts sometimes are used in the assembly of plastic parts with standard screws.

Though inserts in molded plastics have decided advantages from the standpoint of simplicity of handling and easy location of attachment points, self-tapping screws may reduce costs of unit pieces if the inclusion of threaded inserts complicates the mold excessively. When loading operations on multiple-cavity molds are slowed down by inclusion of threaded inserts, there is the possibility that external attachment screws may expedite production. In addition to self-tapping screws are drive screws which are designed primarily for permanent assemblies and are not easily

withdrawn from an assembled article. Tapping the holes in molded plastics is slow and costly, and does not give as finished a job as self-tapping screws or metallic drive screws. Against the alternative of tapped holes in the plastic materials using standard threaded parts, must be weighed the more mechanically secure, though more costly self-tapping or metallic-drive screws. A summary of the methods of attachment includes:

1. Drilling a hole completely through the piece and using a through screw with lockwashers and nuts
2. Tapping a thread in the material and using a machine screw
3. Using self-tapping or metallic drive-screws
4. Using studs molded integral with the plastic, accompanied by self-locking speed nuts
5. Use of strong, gap-filling adhesives.

The first method may be unsatisfactory from an appearance standpoint, though it may be least costly in some assemblies. Tapping threads in fibrous molding compositions or fabric-base laminated plastics does not always yield good results as threads may be weak and incomplete. Provided sufficient thickness of material exists, good mechanical connections are obtained through the medium of self-tapping screws. Connections of this description have appeared on terminal strips, switch panels, clock housing assemblies, knobs, covers, and nameplates. Difficulties are encountered, however, for the more brittle urea plastics.

Speed nuts have come into prominence in dozens of assemblies of plastic parts. Pushed into position about some plastic stud, speed nuts formed of hardened spring steel are quickly assembled, serving to secure the assembly under a certain amount of spring tension. Attachments of this nature compensate for creep in the plastics.

Chapter XI

Characteristics and Preparation of Molding Compounds

Of fundamental interest to all engineers are the phenomena which take place during the hot molding of plastics. Thermosetting plastics are particularly intriguing because of the complete physical and chemical changes which take place in the materials at the time of molding. The manufacturers of materials bring the thermosetting molding compounds up to a stage of polymerization which requires only the application of heat and pressure from the molds to convert them into useful articles. In this heat-reactive stage the compounds are susceptible to many influences which can affect their molding qualities, and proper care must be exercised to obtain the optimum molding performance. A brief review of the many factors which influence the molding properties of the materials will throw some light on the phenomena involved.

Thermoplastic molding compositions of cellulose acetate, methyl methacrylate, polystyrene, ethyl cellulose, etc., do not experience the profound changes of the phenolic and urea compositions during molding. Nevertheless, these materials may not be handled promiscuously if good molding and good properties are to be obtained. Thermoplastics are essentially in their polymerized form when the custom molder receives them, though the presence of plasticizers or monomeric forms of the resin are necessary to insure adequate flow during molding.

Of paramount importance to custom molders is the time of the molding cycle. While the selection of molding materials is contingent primarily upon the properties desired in the final articles, the behavior of the compounds during molding must be analyzed in order to ascertain materials and conditions for an optimum cycle. As will be brought out later in the chapter, the molder is in a position to improve upon the efficiency of his molding cycle through appropriate materials preparation such as preforming and preheating.

Physical Forms of Molding Compounds

Molding compounds are prepared in a number of physical forms, the selection of which often are dependent upon the methods in which they are to be handled. Some of these forms together with a short description of each, appear in the following paragraphs:

Powders: The phenolic, urea, and melamine formaldehyde molding materials generally are sold as powders. The powders usually comprise a small percentage of fines capable of passing an 80-mesh screen, though the greater proportion are of larger size. From the standpoint of bulk factor and ease of feeding through chutes of preforming machines or automatic presses, coarse granules are preferred. Thermosetting materials generally are ground to pass a standard No. 12-mesh screen, though this does not apply to fabric-filled or cord-reinforced compositions.

Granules: The tougher thermoplastic molding compounds are not easily reduced to powdered form. For molding purposes the granules are preferred because they feed more easily on injection and extrusion machines. The granules are as large as 3/16 to 1/4 inch. In fact, some grades of cellulose derivatives are available almost as perfect ⅛-inch cubes, die-cut to the correct size. During the emulsion polymerization of styrene or methyl methacrylate, large globules or spheres have been formed, which also are suited to ease of feeding the machines, though finely divided spheres may be obtained if required.

Resin-Impregnated Sheets: Resin-impregnated sheets of paper fiber or resin-impregnated sheets of creped paper are popular in compression molding plants. While limited in flow, they nevertheless contribute markedly to the strength of thin-walled objects or at points of severe stress. Creped-canvas-impregnated sheets also have been developed to improve flow during molding. Trays, refrigerator door strips, and instrument cases are a few of the many examples.

Resin-Impregnated Pulp Preforms: From wet slurries of resin and pulp fibers, vacuum screens are employed to pick up resin and pulp pads or preforms which approximate the mold dimensions. This activity is new, but it promises to be a very important one when molding large contoured articles, as very strong and durable moldings are obtained.

Best results are obtained upon phenolic resin-impregnated pulp preforms with beater-dispersed resins. Under these conditions the resin is adsorbed upon the surface of fiber rather than into the material. In consequence very much higher impact, tensile, and flexural strengths are realized.

Pads of Resin-Impregnated Fibers: Pads of phenolic resin-impregnated sisal, cotton, or glass fibers have served the molding industry. High impact strength and low molding pressures generally characterize these developments. From droppable fuel tanks to handles for instruments these compounds have shown their versatility.

Molding Blanks: In compression molding of thermoplastics, particularly where large flat areas are involved, sheets of thermoplastic molding compound may be die cut to the approximate mold size. This will reduce the time of molding and insure an adequate, uniform distribution of material about the die. These sheets, however, are appreciably more costly than the molding granules or powders. Representative material costs are given at the end of the book.

Behavior of Thermosetting Compounds During Compression Molding

When a thermosetting material is introduced into the mold cavity and the mold halves close together, several factors determine the rate at which the material is brought up to the molding temperature:

1. Temperature of material when it is introduced into the mold
2. Bulk factor of the material
3. Thermal constants of material (thermal conductivity and specific heat)
4. Rate at which the molds are closed
5. Ratio of total surface area of article to volume of material
6. Molding temperature (average) throughout surfaces of the mold.

Some of these factors are controllable for a particular operation—temperature of material, bulk factor, and molding temperature. The others depend upon the design and the composition selected. While it is true that the rate of closing the mold

may be reduced if the material is preheated, the fundamental factors determining the rate of closing depend upon the nature of the design, inserts employed, the reactivity of the particular molding compound, and resistance of the compound to the mold-closing pressure.

Under the application of heat and pressure, condensation-polymerization proceeds at a rapid rate in the thermosetting compounds forming the complex high-molecular-weight polymers which constitute the final molded product. The mechanism of this polymerization was reviewed in Chapter II. The molding material during this process resembles a highly mobile fluid, capable of flowing to all parts of the mold and reproducing the designs. However, as polymerization proceeds the viscosity of the resin polymer rises rapidly until a point is reached when the material takes a definite set, such that continued application of heat and pressure will only serve to further the polymerization and the degree of infusibility of the material. After the material has set, a further curing period is necessary to develop the optimum physical and chemical properties.

While the basic phenomena in the molding of thermosetting compounds may be explained in terms of polymerization and molecular configurations, it is the practice of plastics engineers to examine molding compounds by empirical tests designed to show the amount of plastic flow, the rate of plastic flow, and the time duration of flow. These properties not only depend upon individual variations among the molding compounds, but they also are dependent upon molding variables of time, pressure, and temperature. In *Fig.* 89 these three variables are shown and a thermosetting compound is compared with a thermoplastic compound. It will be noted that the rate of flow of a thermosetting compound may in fact be quite high, though once cross-linking begins to take place the material sets up and no further flow takes place. When flow has ceased the material is cured further until the optimum physical and electrical properties are developed.

Evaluation of Flow in Molding Compounds: Molding characteristics should be evaluated at different pressures, at different temperatures, and for different intervals of time. At least one method has been standardized upon (ASTM D-569 "Flow Temperatures of Thermoplastic Molding Compounds"), where a $\frac{3}{8}$-inch diameter preform of molding compound is placed under constant

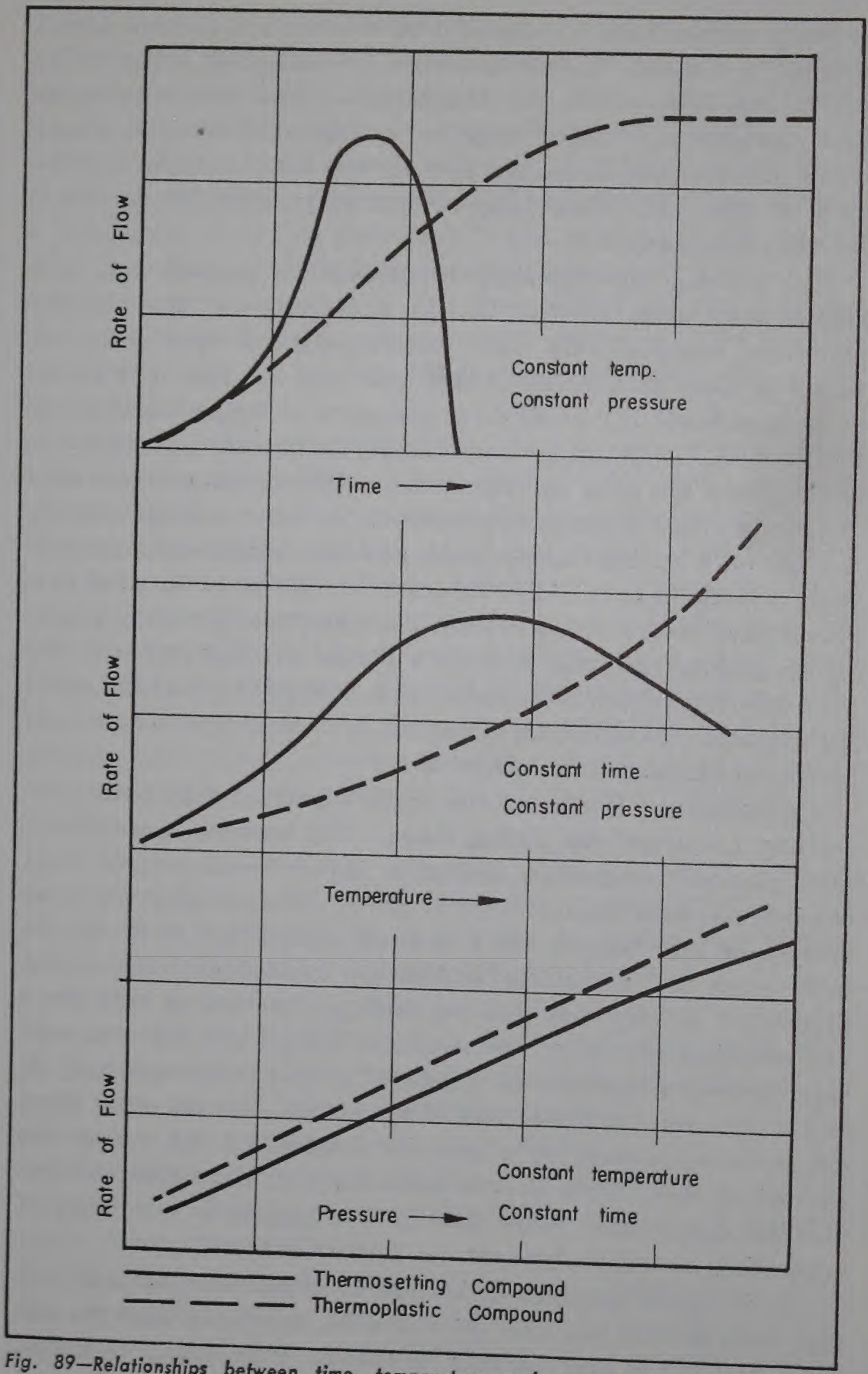


Fig. 89—Relationships between time, temperature and pressure in the molding of thermosetting and thermoplastic compounds

pressure derived from a series of dead weights, and the flow traced through a constant ⅛-inch diameter, 1½-inch long orifice. The ASTM flow temperature for thermoplastic materials is taken as that temperature (which may be extrapolated from a chart) where the material flows one inch in two minutes under a pressure of 1500 psi. Flow temperatures vary from 250 to 350 F for most thermoplastics.

In molding thermosetting compounds no method has been standardized upon as yet, though a majority of the phenolic materials manufacturers base recommendations upon data obtained in units such as the ASTM split-cone one described above, examining flowability at different pressures at temperatures about 300 F. Other empirical methods include the flow through an orifice directly into the open air, where the weight of material extruded at different time intervals is measured. Another technique entails the use of a multiple-cavity mold, and the determination of how many cavities may be filled in order for the press to close in a stated time interval. Cup flow tests are preferred for ureas whereby the molding material is given a partial molding pressure, and then held for various intervals of time, followed by final full molding pressure. Examination of the cup or tumbler produced affords additional data on the flow properties.

Temperature is one of the most important influences upon molding properties and curing times. For example, a woodflour-filled phenolic composition molded at 300 F would cure in about one-half the time when molded at 350 F. Molded ureas are more critical, as cure time at 290 F is about double that at 310 F. In fact, ureas and melamines seldom are molded at temperatures over 320 F as they may cure too rapidly. The flow of both ureas and phenolics are affected by moisture, though in a different manner. Excessive exposure to moisture for urea compounds may effect a premature cure and loss of flowability. On the other hand, low moisture content in a phenolic composition will reduce the amount of flow. This is even more apparent for lignin enriched phenolic compounds. Cure time is also subject to conditions of preheating, as will be brought out further in the chapter.

It is highly desirable to be able to obtain compositions with fast rates of cure and slow rates of cure, depending upon the size to be reproduced and the wall thickness. Pure phenol-formaldehyde resin with appropriate amounts of hardening agents pro-

viding a surplus of methylene groups will cure quite rapidly. On the other hand, the inclusion of cresols and xylenols will slow cure down appreciably. There are not many true plasticizers for the thermosetting phenolic compositions, except perhaps certain derivatives of cashew nut shell liquid such as cardanol, which is a form of phenol. Practically all the plasticizers may exercise a temporary benefit in promoting a greater rate of flow at the time of molding, though their presence does not necessarily contribute to any toughening of the final molded product. Among the ureas, various flow agents have been developed to prolong the flow, particularly for large moldings where slow mold closing time is essential.

Influence of Design: It usually is necessary to experiment with molding compositions before entering production, to determine the optimum mold temperature and sometimes the best suited of several available compositions for a particular design. Large machine housings, for example, will require compounds with a long duration of flow and extent of flow so that the materials will flow satisfactorily to every part of the mold. Smaller articles, which are relatively simple in design and shallow in depth, may require a good average flow and a rapid setting time for economical production. Plunger molding techniques afford effective means of decreasing the cure time for quite a variety of small articles.

Temperature gradients may exist from the steam ports to extremities of the mold construction, and pressure gradients will depend upon the disposition of preforms or powder with respect to the force plugs. This is borne out by evidence of variation in mechanical properties and nonuniform density in molded articles. Though not always attained, it is desirable that at some stage of plastic molding, all the molding material be under flow at the same time, thus tending to distribute stresses more evenly. The influence of the individual design upon the heat transfer rate cannot be under-rated, because the flow and distribution of molding material is a function of the mold surface areas, their temperatures, and molding pressure.

The minimum curing time of any one thermosetting molding composition under certain conditions of pressure and temperature, is that time required to bring about practical completion of the chemical reactions, such that further applications of

heat and pressure to the molded piece would be inconsequential in the improvement of physical properties, infusibility and insolubility. Stated in another manner, the minimum curing period is that time necessary to give the thermosetting material its nominal physical and thermal properties and resistance to chemicals. The curing period for thermosetting plastics extends beyond that time when the material ceases to flow under pressure in the molding dies.

Various indices for indicating the minimum cure are through acetone extract test methods, whereby the amount of soluble, Stage B resins is determined by adding a portion of a pulverized molded piece to the solvent, and measuring loss in weight of remolded piece. Another criterion is the appearance of blisters resulting from the internal gas pressure. When the thermosetting compound has been molded such that the surface is sufficiently rigid and will not give way under internal gas pressure and blister, adequate cure has been realized.

Certain slow molding compositions with a relatively large moisture content will require long periods of cure. It is not only uneconomical to carry the cure for too great a period, but there is a possibility of burning the piece. This is one reason why wide variance in wall thickness of the molded piece is a poor design feature, as sufficient cure for a thick section may be excessive cure for a thin portion. Because of the low heat conductivity of plastic materials, thick sections (in excess of ¼-inch) cannot be molded at too high a temperature to avoid overcuring of the surface during the time lag in heating and curing of the innermost sections. Hence the curing time is greatly increased, except when some of the more recent methods of high-frequency and high-humidity preheating are employed.

A rapid test for evaluating the cure of small sections of molded phenolic or urea molding compounds is through the aid of a punch and die mounted upon an arbor press. Punch strength may be readily plotted as a function of the cure time. In discussing variables influencing the properties of plastics, this feature was examined in the chapter on physical properties. For ureas, a boiling water test has long been standard, whereby the molded parts are immersed for 10 minutes. If they turn chalky it is definite indication that they have not been cured to a sufficient extent.

Behavior of Thermoplastic Molding Compounds

Thermoplastic molding compounds involve molding problems differing appreciably from those of the thermosetting materials. Fully polymerized when received by the molder, they are not as critical in their temperature and time during hot molding.

Most thermoplastic materials may be molded by injection and extrusion techniques. There is a limit, however, on the time they may be safely kept at molding temperatures, because of tendency for plasticizer separation to occur or because of changes or loss of low molecular weight fractions due to some decomposition. Successful injection molding and extrusion at temperatures varying from 350 to 450 F depend upon continuous flow and movement of the material through the plasticizing chamber of the molding machine. The setting or hardening of the thermoplastic compounds takes place in the mold due to the cooling action of the mold surfaces. Mold temperatures usually are kept close to room temperature by cooling water, though some materials such as polyvinylidene chloride are best molded into molds near 200 F. This arises from the fact that Saran, if chilled too quickly retains its soft, amorphous state, whereas at temperatures of 160-200 F, it recrystallizes to a hard consistency, capable of being safely ejected from the molds.

The high temperatures for plasticizing the materials may introduce special problems for the injection molding machines. For example, materials such as polystyrene acquire such low viscosity as to require close-fitting injection plungers and cooling means to prevent any backing up of the molding material toward the hopper. Polyamides, in particular, offer difficulty. They are molded at temperatures from 510 to 550 F and require a special valving at the nozzle of the injection molding machine to prevent excess loss between cycles. Other materials such as the chlorinated polyvinyl copolymers require corrosion resisting steels for the plasticizing chambers, otherwise hydrochloric acid formed from decomposition products may corrode the heating chamber.

Preforming of Molding Compositions

Molding may be conducted economically and at a much more rapid rate when the molding charge has been correctly ascer-

tained prior to introducing it into the mold cavity. When thermosetting compounds are employed, excess flash represents so much wasted material, whereas with thermoplastic types, the material may be re-used if not contaminated or burnt. The careful accurate weighing of the charge is essential to avoid wastage of material in the flash or an undercharge. The effects of an undercharge are displayed usually in an incompleted molded article or mechanical weakness in the molded part.

Experience of custom molders is that considerable savings may be effected by establishing accurate methods for measuring the correct charges for the mold cavities. Allowances for excess flash are about 5 per cent of the total charge, though through improper material preparation this may run even higher. When the amount of work being handled warrants extensive planning, it may be of advantage to have a separate department whose sole function is to weigh out powder and count preforms.

While powders may be economically employed in large single-cavity molds or in large flat castings where there is relatively little flow of material, there are many advantages accruing through the use of tablets or preforms for multiple-cavity molds. Preforms are not only easier to handle than the bulk material, but also, as pointed out later, will simplify the problem of measuring the mold charge accurately. Operators engaged in running the presses find it more convenient to count tablets and place them in loading trays or fixtures for filling the multiple mold cavities at the start of a new molding cycle. However, in some jobs, molding powders are either necessary or may not be avoided because of the nature of the material. To reduce the labor of weighing out each charge, automatic weighing machines can effect economies and insure uniform results.

A further noteworthy distinction between molding powders and preforms or tablets is in the bulk factor of the material, which is much higher for the powder. Bulk factor is defined as follows:

$$\text{Bulk Factor} = \frac{\text{Volume of loose powder}}{\text{Volume of molded piece and flash}}$$

$$= \frac{\text{Specific gravity of molded piece}}{\text{Apparent specific gravity of powder}}$$

In Table LI of the next chapter are listed the bulk factors of various molding materials. Preforming or tableting reduces these values to about 1.5 to 2.5. This means, for example, that the loading cavity of a mold for a material with a bulk factor of 5 may be reduced by one-half, by preforming. In summarizing the advantages to be expected from tableting and preforming, there is the following:

1. Bulk factor is reduced
2. Depth of the mold is reduced because powders are more compressed
3. Ease of handling the molding charge by operator
4. Thermal conductivity of compressed piece is better than loose powder
5. More advantageous allocation of molding composition in mold, accompanied by improved flow.

Tableting: Tableting of molding powders is conducted usually in automatic machines containing single or multiple-cavity molds. The powder is compressed to a tablet of known density and weight, with a diameter and depth suitable for the intended mold. The tableting operation is analogous to cold molding without adversely affecting the flowing or curing properties of the thermosetting materials. By having a tablet of known size and weight, handling of the loose charge is avoided and operations greatly simplified. The molds for preparing these tablets are not highly polished, full final finish being obtained on the molded piece in the regular production mold.

Molds are charged with one or more of these tablets to attain the desired results, though powders sometimes are used in conjunction with tableting. Sometimes the material is made available in pellet or pill form, for convenience in handling and accuracy of weight. Pellets are smaller than tablets and when being charged into the mold a specified number are added. These, as well as the tablets, are suited to miscellaneous mold forms, instead of being designed for any type like the preforms described later. The weight tolerance for the mold charge is plus or minus the weight of the one pellet, and it is preferred to favor the plus and spill a little through the flash, rather than take a chance of rejection by undercharging a mold. Pellets in the form of small balls are easy to handle and to load.

Tableting methods are not suited to certain types of molding powders which are limited in their capacity for preforming or tableting. Special reference is made to the long fiber asbestos or mascerated fabric-filled thermosetting plastics. Their drawback occurs in their lack of ability to slide down the hopper and feed shoe into the cavity. Pulverized wood-flour fillers, powdered mica fillers, and certain others are filled readily in the mold cavity. For long fibrous materials, it becomes necessary to weigh the molding compositions and introduce them into the mold in powdered or granular form. This is one of the reasons for the higher cost of these compounds and their molded products. When the material becomes too fibrous to handle rapidly and economically in the tableting machine, the compositions are compressed by hand in cold-molding operations. This will reduce the high bulk factor of such materials as canvas-filled phenolic compositions, which may be as high as 8 to 10 to 1. Mold costs for handling this volume run high, and it is sounder economy to preform, even though it is a hand operation.

Where there are large quantities of fabric-filled molding compound to be tableted, special machines have been developed (Kux Machine Co.) for metering out and tableting these materials. These machines are a new development and of more elaborate design than the conventional single punch affair for general-purpose materials.

Also of note are tableting operations upon urea plastics. Granular compounds are preferred to the fine powder in tableting ureas, as they may be handled more easily in the preforming equipment. The bulk factor of the granules is about one-half of that of the fine powder, which is 4.9. In tableting these materials, the machines are housed in separate rooms. This practice is followed in order to avoid contamination of light pastel shades by dust and dirt of darker materials.

Some manufacturers have set up their own standards in classifying the relative ease with which different molding compounds lend themselves to the tableting operation. In general, the longer fibrous fillers retard the passage of molding materials down the hopper of the tableting machine, and will not preform readily. The types of molding compounds are classified as follows:

Class I—Readily preformed on automatic tableting machine

Class II—Similar to Class I, except that special attention is given to the molding material to improve the feed
Class III—May be tableted with difficulty, requiring special hoppers and feeding devices
Class IV—Will not feed, requiring the formation of tablets by hand.

Among other factors which will influence the firmness and soundness of the preform outside of the quality of the molding material, is the size of the piece and the pressure applied. Lack of adequate density is manifested by preforms which will crumble easily. This may be due to insufficient material fed to the die, or even compounds which are cold, such as those newly received in winter shipments. Changes in the bulk factor of the material which occur when the fines tend to separate from the granules also cause difficulty.

Preforming: Analogous to tableting operations, and performed in the same type of machinery, are the preforming operations upon molding compositions. This time, however, preforms are shaped to suit a particular mold cavity or insert. A large variety of knobs, buttons, dials, and miscellaneous small pieces are prepared first in the form of preforms, which closely approximate the ultimate external dimensions. They generally are designed smaller in overall width to provide an easy fit, though thicker to provide adequate material to fill out the mold. Sometimes, the preform may be supplemented advantageously by small pills or pellets which may be placed in deep recesses or about core pins which tend to distort during molding.

Preforms in the shape of rings have been well suited to the simplification of molding operations upon long, horizontal cored pieces. The preform rings are slipped over the core pin and stacked to the proper width. Molding will unite the entire mass into one compact unit. Square, tubular, miscellaneous geometric patterns of every description constitute the types of preforms available. Complicated shapes are avoided because they represent extra mold expense, and the shapes of preforms are confined to relatively simple forms.

Volumetric Loading: Volumetric determinations of molding charge are employed currently for hot and cold-molding compositions. Materials that do not tablet are sometimes measured volu-

metrically. In cold-molding operations, the operators are furnished with a rake at the molding press with which they may reach into a hopper behind the press and fill up the mold cavity between cycles. The mold cavities are leveled off and volume determines the amount of charge. This inexpensive, though not-too-accurate method of obtaining cold-molded charges, leads to inaccuracies in the final dimensions parallel to line of molding pressure. Vertical dimensions are those most profoundly affected by the inaccuracies of charging, particularly if an insufficient amount is employed.

Equipment: The machinery and equipment for the manufacture of preforms and tablets for molded plastics fall into one of two classifications of machines, both of which are shown in *Figs.* 90 and 91.

1. Heavy-duty, single punch preforming machine. This press is best suited for large tablets, small production quantities, special shapes, and general work in the molding establishment. Typical units of this description have preform diameters up to 3 inches and maximum depth of fill up to 2 inches. The molding pressures usually are 10 to 15 tons, some units having as high a capacity as 150 tons.

2. For rapid, high-quantity production of small tablets, a rotary press has been developed. Because of the large number of punches and dies employed, the rotary press can turn out as many as 600 to 800 tablets per minute. Small ball or convex-shaped pieces are molded most economically, several being used to one large tablet. A typical machine may contain 24 die sets for $1\frac{7}{16}$-inch diameter tablets. Pressures on such machines are available in 10 to 15 tons. Some rotary presses with larger capacity are available with molding pressures up to 30 tons.

The automatic features of the preforming operations are highly interesting. In the rotary press, a revolving table with a series of die holes progressively locate the dies beneath the hopper feed shoe, the spout withdrawing after filling the die with molding material. The table then rotates the die to the molding position, while another die replaces the first under the hopper feed shoe. Stationary baffles wipe off the excess molding compound position after each filling to the level of the die. Adjustments for the various preforms are made easily and rapidly. By dropping down the lower punch, which receives the material, thicker sections can be preformed. Slow compressions from the upper

and lower punches by suitable cams in the preforming machine is deemed an advantage in obtaining a preform of more uniform density.

Slow compressions of the rotary press avoid the rapid stroke of the single punch press and the sometimes unsatisfactory mold preforms which readily crumble or de-laminate when proper operating conditions are not observed. The application of pressures

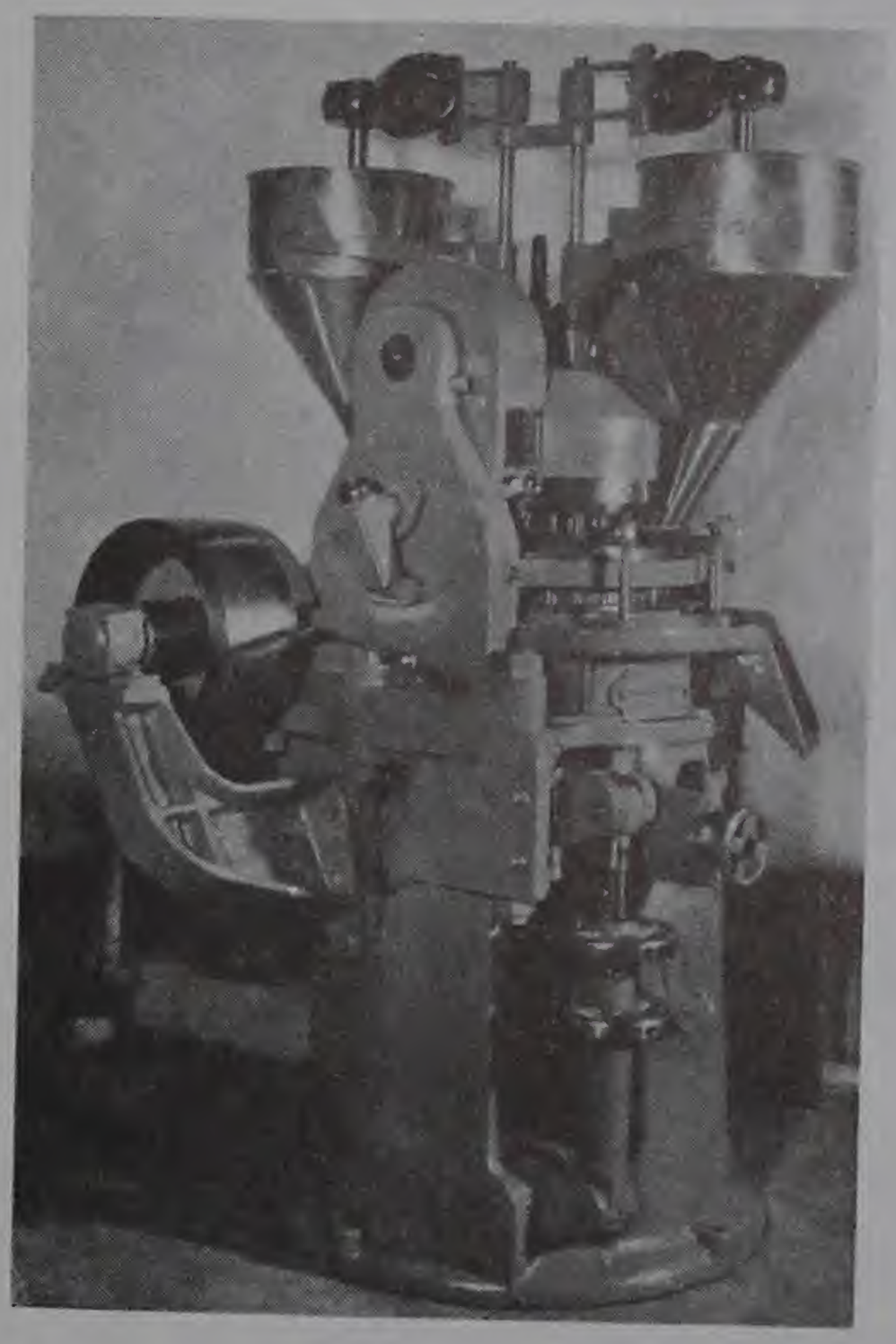


Fig. 90—Double-sided rotary press to preform pieces up to 1¼-inches diameter (Stokes Machine Co.)

at a more gradual rate has been well suited to preforming urea compounds. Release of compression pressure is followed by the upward movement of the lower punch to eject the preform. The mold cavity is cleaned out by blowing and made ready for the next refill. Some machines are equipped with automatic devices to release pressure in the event of jamming.

Uninterrupted operation of preform presses usually is demanded in molding establishments working at top speed. Delays by jamming are apt to be costly, and when the molders sometimes adjust the machines for pills of one density, changes in compression ratio of the molding compositions may cause jamming. These changes may occur particularly when the vibration of the ma-

chine causes the finer and more dense particles to segregate from the more porous pieces in the feed hopper. Portions of previous tablets left behind also may cause jamming.

Rotary presses sometimes are operated with several distinct pairs of dies and punches to give preforms of different shapes.

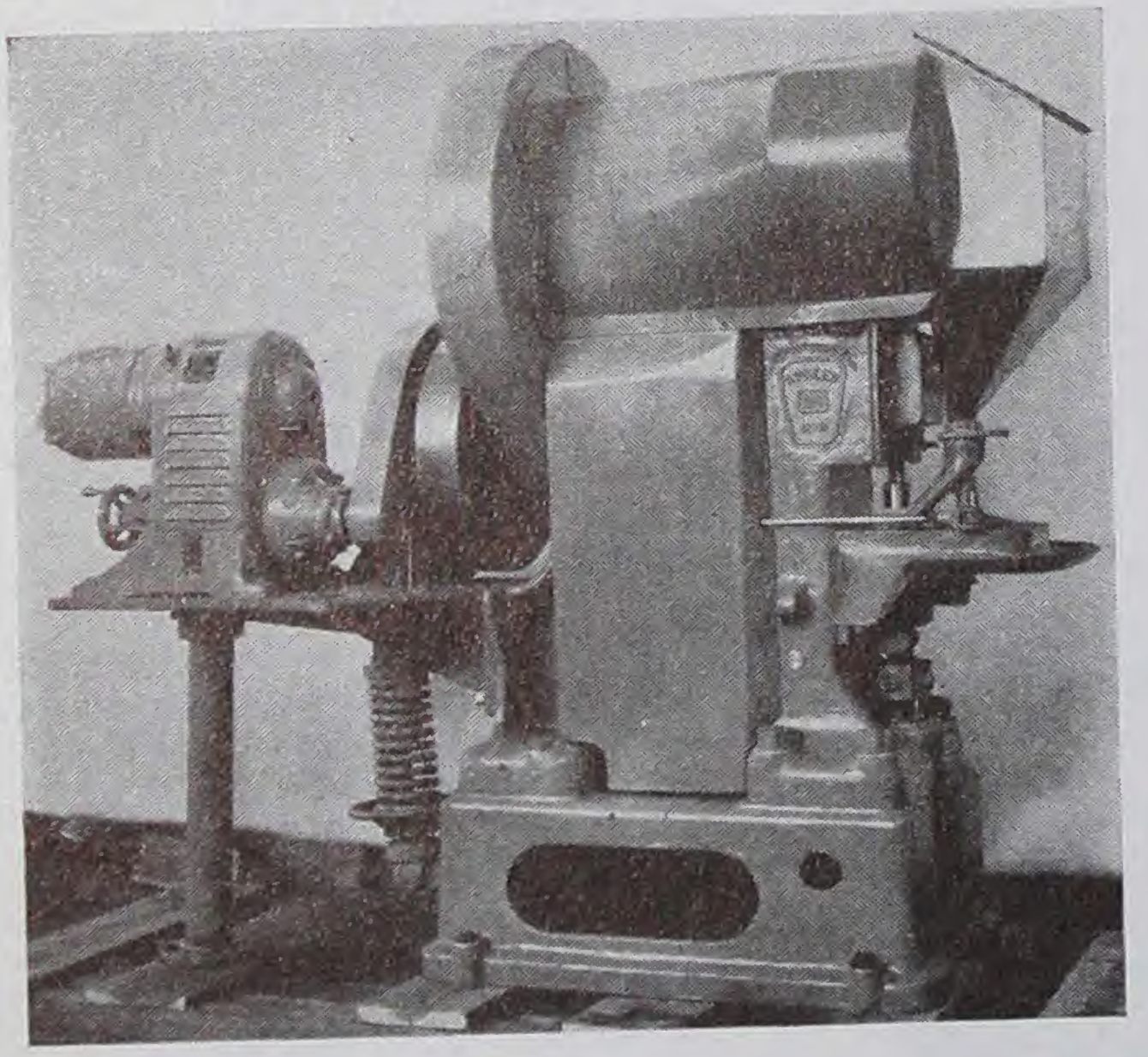


Fig. 91—Preforming press for pieces up to 2½-inches diameter, driven by variable-speed motor (Stokes Machine Co.)

Requirements of several jobs may be fulfilled in this manner, though individual preforms may have to be separated manually. This rapid change-over from one die to another speeds up the production of odd-lot quantities from rotary presses. Two cavities on single-punch presses also have been used, whereby more than one die is fed by the feed shoe. Though production is increased, it is claimed that distribution of material from the hopper has caused lack of uniformity in preform due to the fact that the cavity nearer the feed shoe received the denser particles.

Punch and dies must be in good shape for preforming operations. Dies must be scraped clean by lower punches, which also should receive periodic attention and expert care. In designing the preform die, there must be adequate clearance around the top punch to permit the escape of entrapped air. Approximately 0.006-inch per inch clearance is the allowance around the punch.

Preheating

Proper, controlled preheating of molding compounds before placing the material within the mold has become one of the most useful adjuncts to the molding operation. Preheating methods have experienced a remarkable evolution during the past ten years, commencing with the hit or miss technique of placing preforms on hot steam plates, to temperature-controlled ovens and, finally, high-frequency preheating and high-humidity preheating. The latter techniques, developed shortly after the start of the Second World War, have, in the opinion of many molders, revolutionized compression and transfer molding practices.

Preforms of molding material are at best poor heat conductors, and by raising them closer to the molding temperature before placing them in the mold many advantages accrue. There are limitations, however, of time and temperature. The higher the temperature to which they are raised, the more rapidly they must be molded, otherwise they may set-up prematurely and flow will not occur. The methods of preheating molding materials are described herewith:

Controlled Oven Temperature: Before the advent of high-frequency preheating, the standard method of preheating molding compounds was through the use of a temperature-controlled oven. A full thirty minutes usually was necessary before the preform would become thoroughly preheated, and the molder usually placed a large number of preforms in the oven to accommodate the more frequent molding cycles. For loose powder which did not readily preheat, special containers with hot oil-circulation jacket, or means of rotating them in an oven were devised. In this manner, phenolics usually were preheated to molding temperatures around 200 F and ureas were preheated to temperatures of about 170 F. At these temperatures, the materials could be left for long periods without premature setting-up. An appreciable reduction of the time of cure was achieved through this preheating, as well as some reduction of mold closing pressures and time.

Preheating of thermoplastics by this method is still widely employed, though for an entirely different purpose. Thermoplastic molding granules are spread out over trays in an oven with air circulation at 140 to 150 F for a few hours, or else exposed to

infra-red lamps. The moisture is substantially removed by this process and clarity of the final product, as well as minimizing of flow marks are assured.

High-Frequency Preheating: High-frequency preheating equipments are standard accessories in most molding plants. A typical unit for this purpose is shown in *Fig.* 92. Most of the

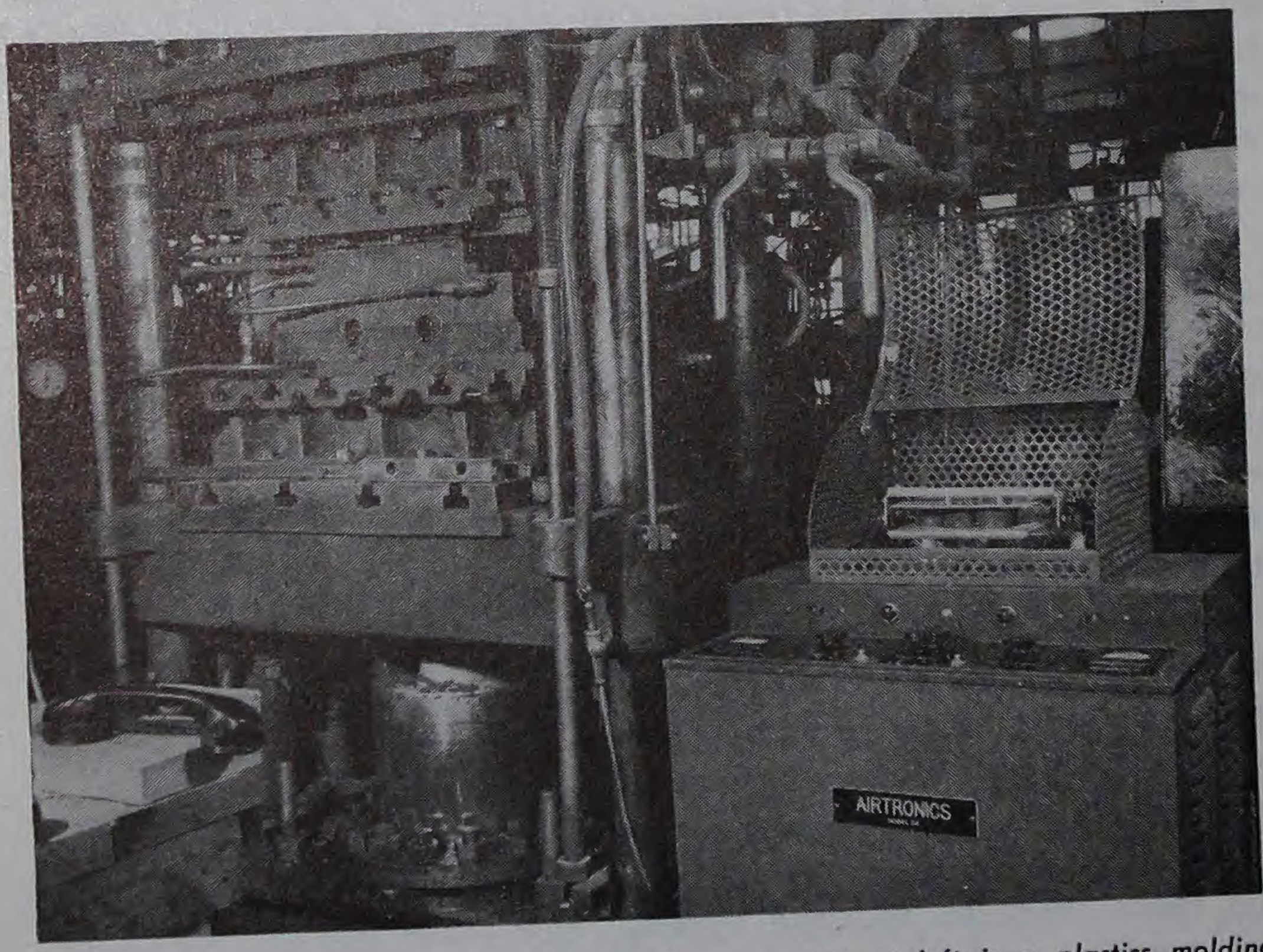


Fig. 92—Unit at right is high-frequency preheater. Unit at left is a plastics molding press in closed position

machines are rated at 1.0-kw output and higher. The principle of high-frequency preheating of molding materials depends upon the power factor and the loss factor of the molding compound. The higher these values, the greater will be their tendency to absorb energy and heat up when exposed to an electrostatic field of high frequency. This heating effect may be explained as a result of "molecular friction" caused by rapid fluctuations of the high-frequency field. Heating occurs directly within the material. The rate of heating of a particular material depends upon its mass, loss factor, voltage, and the frequency. Much of the high-

frequency preheating of molding compounds is conducted in the vicinity of 30 megacycles.

In the chapter dealing with the electrical properties of plastics the rate of heating woodflour-filled phenolics was demonstrated from some laboratory measurements. The factor which every molder considers is the quantity of material which may be preheated within a period of about one minute or at some time less than the molding cycle. The big advantage of high-frequency preheating is that the thermosetting material may be brought up to temperature within the same period of time required for a cycle of conventional compression or transfer molding. While molding temperatures may be attained in the preform, this is never done in practice because most thermosetting compositions would precure or set-up prematurely before placing them in the mold. The preforms generally are preheated to temperatures of 220 to 240 F and then placed immediately into the compression or transfer mold. Among the advantages immediately apparent are:

1. REDUCED MOLDING PRESSURE AND MOLD CLOSING TIME: Because the preheated material may be more quickly plasticized by the hot molding surfaces, mold closing time generally is reduced to a small fraction of the time required without preheating. This advantage becomes more apparent when a large quantity of material is involved, and where a molded piece covering a large area is to be reproduced. Lower molding pressures (40 to 50 per cent of conventional) are required to cause the material to flow properly.

2. REDUCED CURE TIME: It usually is claimed that the prime advantage of high-frequency preheating is reduced cure time. This has been proved time and again, the greatest savings being manifested with thick molded articles. When transfer or compression molding thick sections, it has always been a problem to insure adequate cure of the interior. High-frequency preheating makes this possible. Meharg reported on a series of tests demonstrating the efficacy of high-frequency preheating (Meharg, *Modern Plastics*, 20, 88, March, 1943). One of his curves is reproduced in *Fig.* 93. The greatly reduced curing time for curve C (the high frequency preheated curve) emphasizes the advantages of this process.

3. IMPROVED PROPERTIES OF MOLDED ARTICLES: The fact that

high-frequency preheating insures proper cure of thick molded articles leads one to expect improved physical, electrical, and chemical properties. This is borne out through examination of a thick molded article produced with high-frequency preheating and one produced without this preheating. Further, the amount of shrinkage experienced by the molded part is definitely less.

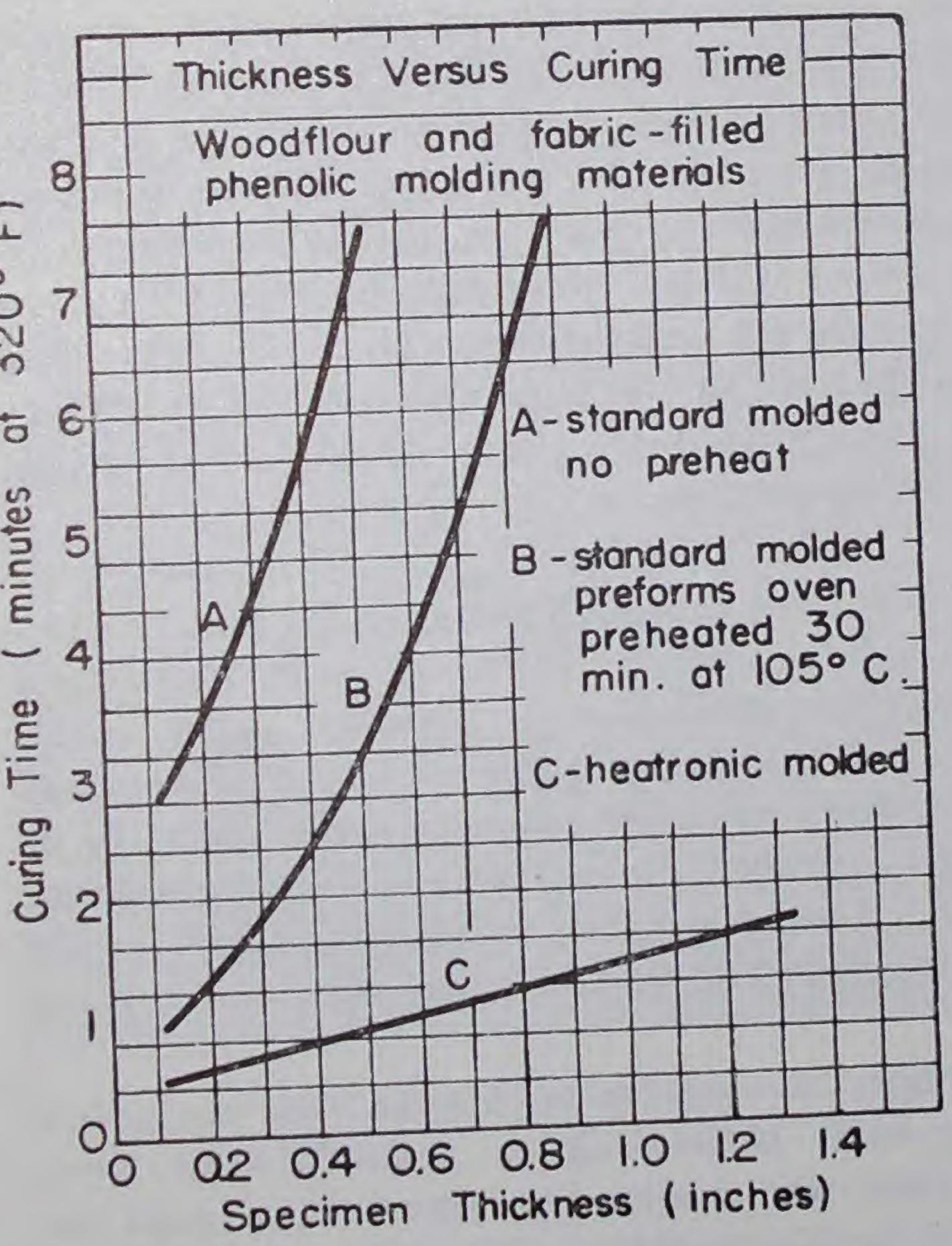


Fig. 93—Optimum times for molding specimens of different thicknesses

High-Frequency Preheating of Thermoplastics: High-frequency preheating of thermoplastic molding compounds has not found much application at present. The rate of heating is slower, due to the low power factors of the materials. Except for high-frequency cementing or heat sealing of thermoplastic sheet stock, this method of preheating has not been used too extensively. However, considerable advantages accrue in processing and vulcanizing rubber stocks by high-frequency methods. Greater adapta-

tion of the technique will be found in this field.

Miscellaneous Accessories: Every custom molder is equipped with miscellaneous accessories to facilitate handling of the molding compositions and their introduction into the mold. Special charging frames containing individual hoppers for each mold cavity permit rapid loading of the molds. Special racks may be designed to remove parts from multiple-cavity molds and air hose to blow out dirt and impurities from the mold cavities before introducing new material. Suitable fixtures and accessories frequently must be designed for each job to expedite handling and molding operations. These would include shrink fixtures and sizing studs upon which hot molded parts are placed while they cool down to room temperature, for the purpose of maintaining accurate dimensions. By proper attention to materials preparations, real economies and high-quality products are obtained.

High-Humidity Preheating: The most recent method of preheating thermosetting molding compounds for transfer molding employs live steam at elevated temperatures. A steam jet is admitted into an enclosed chamber in which the air is kept moving. Preforms of molding compound are placed upon trays and slowly brought up to temperature. The presence of the steam laden atmosphere prevents pre-polymerization, which would occur in a dry oven at the same temperature. Materials thus may be brought close to molding temperature, and are rapidly placed in the transfer pot for molding. Reduced molding cycles comparable to high-frequency preheating are realized without the costly investment in high-frequency equipment.

Of course the live steam preheating technique will not preheat the molding material as rapidly as high frequency, though by preparing enough preforms in advance, their preheating may be adjusted to the timing of the molding cycle. While at first it may be suspected that physical properties of the molded parts would be adversely affected, tests show otherwise, and the technique has been adopted by quite a few molders. Among other advantages of live-steam preheating is the introduction of more moisture into the molding composition. The improved flowability is an asset, inasmuch as the flow is a function of moisture content. However, electrical properties will suffer to some extent.

After Baking: For the greatest dimensional stability of molded phenolic or melamine parts, an after-baking cycle will prove

expedient. Upon removal from the mold, the parts are placed in an auxiliary oven at a temperature of 250-275 F for several hours. Parts continue to shrink, due to a slight additional cure without the restraining pressure of the mold. However, this shrinkage is what would have occurred over many months in service, hence the pieces removed from the after-baking oven will maintain dimensions more accurately. Precision molded parts for instruments and machines are conditioned in this manner.

Chapter XII

Compression and Transfer Molding of Plastics

Manufacturers find use for molded plastics in the design of their machines or products, either as a small component fulfilling electrical, mechanical, or chemical requirements in a large assembly, or as a major component where style and appearance are fully as important as the functional details. It is from these manufacturers that designs in applied plastics originate, and much credit for the advance of the plastics industry must be attributed to their efforts.

When a design in molded plastics once has been chosen and the consumers' requirements as to shape, color, nature of application and cost are understood, the method of molding and the type of material to use are given some study. Inasmuch as the nature of the material and the method of molding have a direct influence on design details, close cooperation between the manufacturer and custom molder is desirable. Changes in the design may appear necessary when the technique of molding the part has been established. These conditions are readily apparent to the engineer who is thoroughly familiar with the properties and preparation of molding materials, methods of molding, construction of molds, and the design principles of hot-molded plastics.

Some idea of the magnitude of compression, transfer, and injection molding may be obtained from the fact that there are close to 900 compression molders in the United States and 550 injection molders. These converters of plastics are occupied in shaping many millions of pounds of molding material each month into industrial goods. Earlier analyses of the industry show:

	1941	1944
Total compression molding machines	8,000	11,500
Compression molding establishments	400	800
Total injection molding machines	1,000	1,500
Injection molding establishments	200	320

In selecting the molding material the custom molder will be governed by two important influences:

1. Attainment of properties requested by the industrial consumer.
2. Utilization of molding materials in an economical molding cycle.

Design engineers, as well as molders, do not have much difficulty in selecting materials to fulfill the properties, unless the conditions are unusual. For the most part, compression-molded phenolics, melamines, ureas, injection-molded cellulose acetates, cellulose acetate-butyrate, ethyl cellulose, acrylics, and polystyrene fulfill the large proportion of the demands. However, suppose, for example, requests are made for a clear, transparent molding material that will withstand at least 240 degrees Fahr. without softening. This requirement eliminates the better known cellulose esters, vinyl resins, acrylic resins, or polystyrene types. The engineer unfamiliar with plastics is uncertain as to the proper selection. Transparent, light amber-colored phenolics which are thermosetting offer some possibility for solution. Newly developed thermoplastics such as polydichlorostyrene and others listed in the chapter on thermal properties will also be acceptable.

Molding characteristics of a given material are understood better by the molder than the design engineer. Due consideration to preheating, preforming, mold breathing, etc., is necessary. Modifications in molding materials as to resin content, fillers, lubricants, catalysts, etc., may be necessary in a standard for new molding conditions. This technique has been outlined in an earlier chapter. Some complicated designs may require a material with a long period of flow in order to reproduce the difficult features of the design, while others may require a short period to decrease the molding cycle. A certain control over properties exists in preheating the materials, molding pressures, and in breathing the mold.

Equally important as the molding material selection is the designation of the method of molding. Certain processes are better adapted to specific resins than others, but in general the choice of hot molding methods will be between compression, injection, and transfer molding. Injection molding and transfer molding resemble one another in certain respects.

The great majority of hot-molded phenol-formaldehyde products are molded by compression or transfer methods, while injection methods are winning wide favor for thermoplastic compositions. Differences of opinion concerning some designs may

arise as to the most satisfactory method of molding. Frequently, two custom molders may disagree over the most economical and satisfactory method of molding a particular part. Both molders may be right, insofar as the most economical method will depend upon the type of molding equipment, fixtures and accessories with which they are prepared to do the job. One may be equipped with modern compression molding equipment, and the other with the most modern injection molding machines. Either molder probably could do an acceptable job. Notwithstanding, proper molding equipment is only a partial solution, while good molds are the keys to successful production.

Compression and transfer molding methods are intimately related to one another. They both have been designed for efficient molding of thermosetting compounds, and they both employ compression molding presses. Differences lie in the mold design and the type of work for which they are suited. In compression molding the material is molded under heat and pressure in the mold cavity which impresses the design details upon the molded parts. Resin impregnated papers and pulp preforms are handled solely by compression molds. On the other hand, in transfer molding the material is brought under heat and pressure in a separate transfer pot, from which the material flows to one or more mold cavities. To assist rapid and efficient transfer molding, the compression pressures are from two to three times greater than for compression molding. Once the material fills out the mold cavity to completion, the cure cycle is substantially the same until the parts are ready to be ejected. However, in plunger molding, which is a special phase of transfer molding, the material acquires additional heat flowing through the runners, and cure is shortened.

Compression and transfer molding of thermoplastics also may be practiced, though much less efficiently than for thermosetting compounds. The materials must not only be heated to the molding temperature, but also cooled down to quite a low limit before they can be safely ejected. The overall cycle time generally is several times that of a thermosetting compound, unless the compression molds have been designed with efficient cooling means. Aside from the production of special transparent varieties not available in thermosetting compounds, compression molding of thermoplastics is not widely practiced. Injection and extrusion

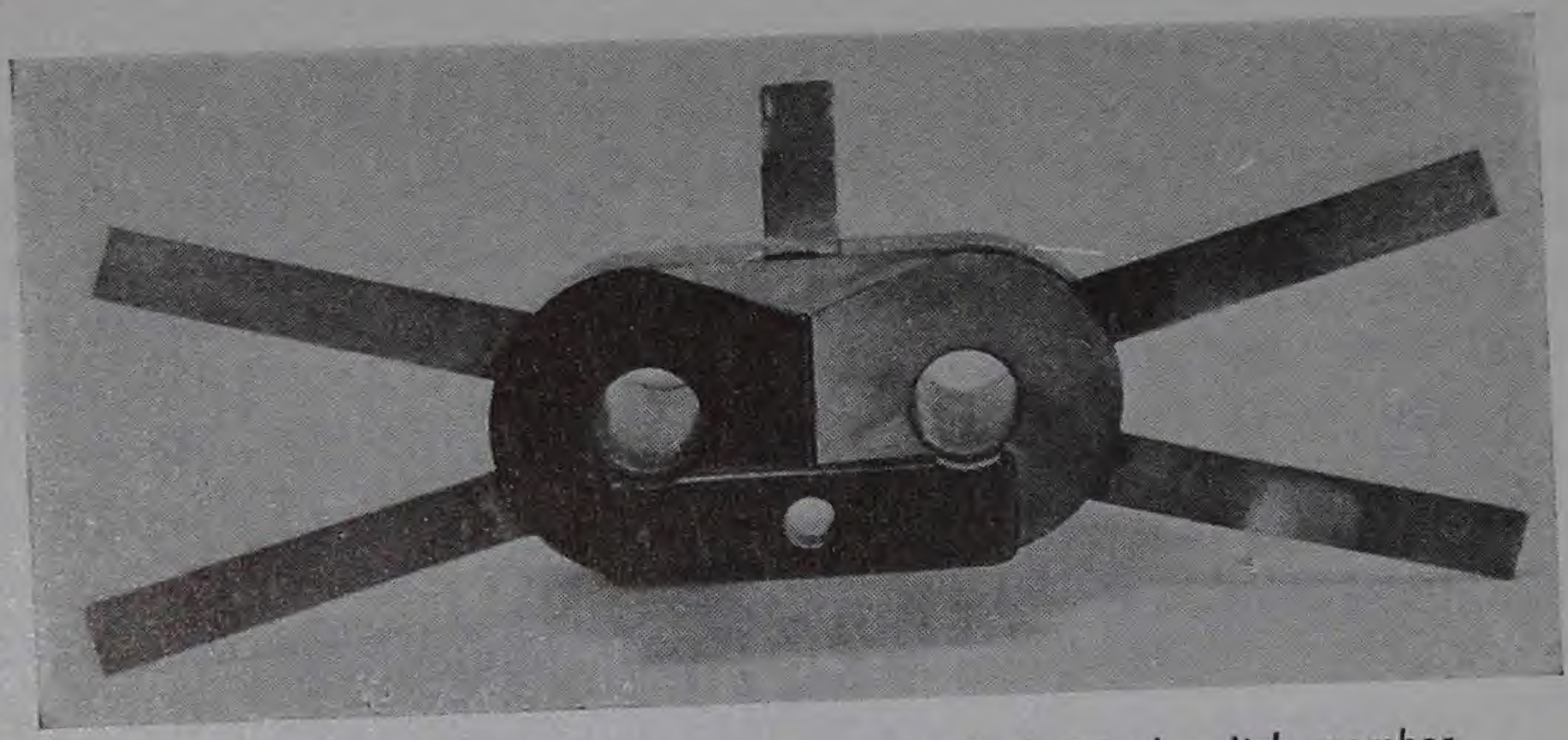


Fig. 94—Large flat inserts—transfer-molded electrical switch member

molding on the other hand, are particularly suited to thermoplastics, and will be covered more fully in subsequent chapters.

The majority of compression molders are equipped to do transfer molding, though the latter process requires a special, nominal licensing arrangement. Transfer molding of phenolic and melamine molding compounds is acknowledged as the best technique

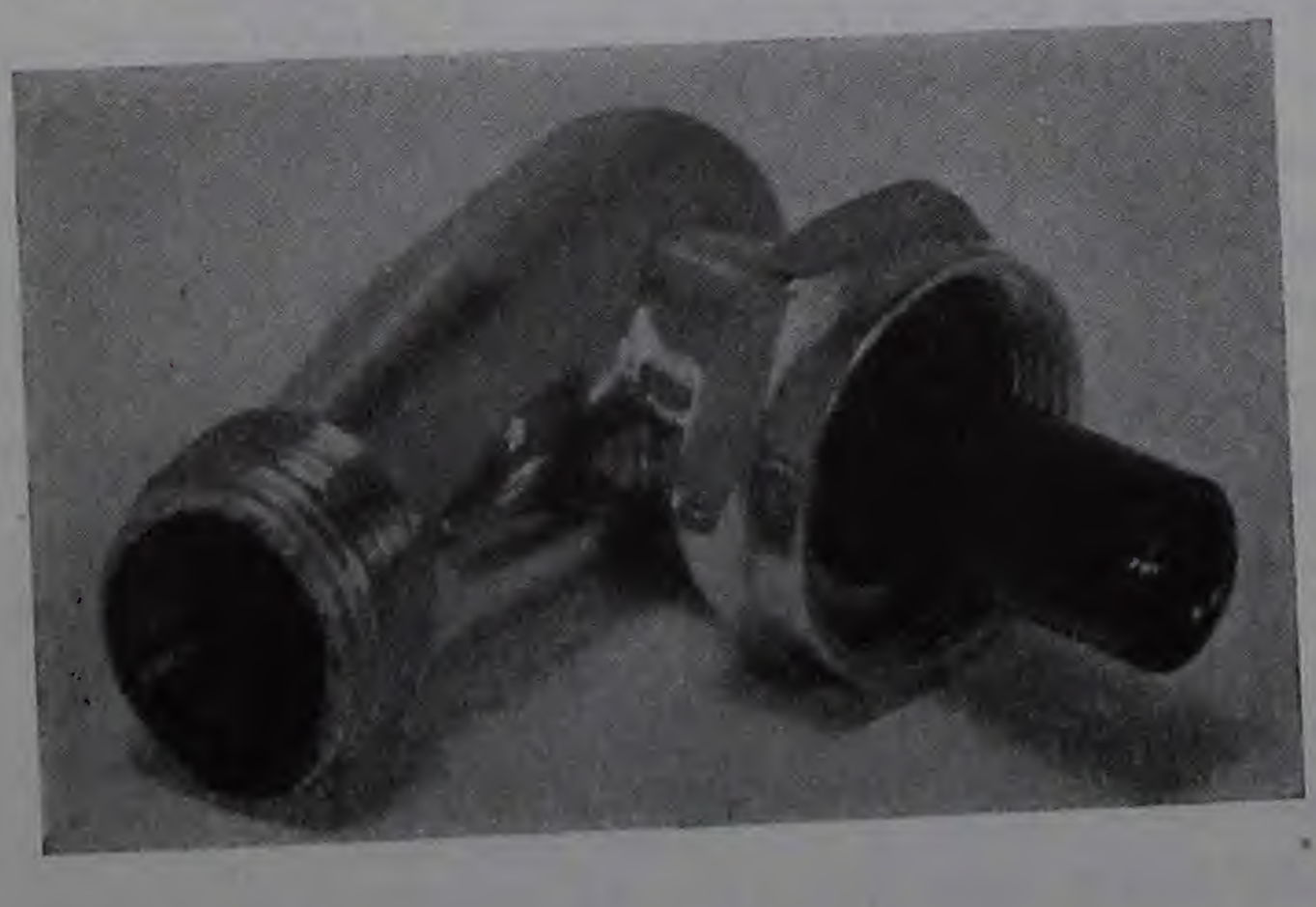


Fig. 95 — Transfer-molded plastic core for spark plug

for molding articles with side and oblique cores, and irregularly spaced inserts. As the material enters the mold from the transfer pot, it follows the path of least resistance, and then, when the mold is filled, the effects of pressure are felt uniformly on all molding surfaces and inserts, with the net result that little or no distortion occurs. On the other hand, in conventional compression molding, as the powder and preforms are crushed in the

mold cavity under the molding pressure, inserts may be broken or dislocated. Typical transfer molded articles are shown in *Figs.* 94 and 95, while a typical molded article produced by compression molding is illustrated in *Fig.* 96. The more intricate, complicated molded parts and inserts are the role of transfer molding, while small simple shapes and very large molded parts are the function of compression molding. At present, only fully automatic molding has been developed for compression molding, due to the simpler mold design, and the ease of removing excess material.

Material requirements for transfer molding differ to some extent from those for ordinary compression molding. Generally, a longer time duration of flow is required, largely to accommodate the time required to transfer the material from the pot to the cavities. In conjunction with high-frequency preheating of the preforms, however, transfer molding is speeded up and a good production cycle may be established. Phenol-furfural molding compounds and long-flow phenol-formaldehyde types with wood-flour filler and fabric filler, are now available for transfer mold-

Fig. 96—Typical compression molded article

ing. As the transfer mold is tightly clamped before the material enters, flash lines are held to a minimum and the amount of cleaning depends upon the amount of the mold wear over many cycles. In summing up the advantages and disadvantages of compression and transfer molding the following facts may be noted:

COMPRESSION MOLDING IS ADAPTED TO:

1. Rapid production of small simple shapes to large pieces covering many square inches of area
2. Fully automatic compression molding in special automatic presses
3. The molding of resin-impregnated pulp preforms and resin impregnated papers.

TRANSFER MOLDING IS ADAPTED TO:

1. Molding of complicated pieces with side and oblique cores and inserts
2. Reproduction of parts with a minimum amount of flash.

Fig. 97—Materials being loaded into transfer pot, preparatory to transfer molding of plug connectors, six of which are shown to left of pot

Stages of Compression Molding

In the following paragraphs the stages of compression molding are examined in some detail. As the material is put under combined heat and pressure, it acquires the properties of a highly viscous fluid, filling out the details of the mold cavities. At the same time, the thermosetting compounds polymerize, undergoing physical and chemical changes to form an infusible, insoluble, structure, which can be ejected from the mold when hot and fully cured. Attention is invited to TABLE LI, listing the compression molding temperatures and pressures of different materials.

TABLE LI

Compression Molding Properties*

Material	Molding: Temperatures (degrees F)	Molding: Pressures (psi)	Bulk Factor
Phenol-aldehydic (woodflour)	280-360	1500-4000	2.2-4.0
Phenol-aldehydic (shredded fabric)	270-340	2500-8000	8.0-12.0
Phenol-aldehydic (asbestos filler)	270-350	1600-6000	3.0-5.0
Melamine formaldehyde	280-360	1000-6000	2.5-3.0
Urea-formaldehyde (alpha-cellulose)	290-325	1500-6000	2.5-3.0
Cellulose acetate	280-340	500-5000	2.0-3.0
Cellulose acetate butyrate	270-340	500-5000	2.0-3.0
Shellac	230-250	1000-1200	2.0-3.0
Ethyl cellulose	320-360	1000-5000	2.2-2.5
Methyl methacrylate	300-350	2000-6000	2.0-3.0
Polystyrene	280-350	1000-3000	2.5-3.0
Polyvinyl chloride-acetate	240-275	1500-2500	2.0-2.5

* Data from bulletins of various materials manufacturers.

The stages of transfer molding are about identical with those of compression molding, except that the material is loaded in a separate transfer pot, as in *Fig.* 97. Pressure applied to the material then flows out to the mold, though the problems of flow, breathing and curing are kindred.

1. CHARGING THE MOLD: Preforms, tablets, pellets, pills, powder, or any combination of these are introduced into the mold cavity by the operator, usually from loading fixtures for multiple-cavity molds. The predetermined, correct number of pellets or a weighed charge of powder are placed in the mold or transfer pot and distributed in a manner which tests have shown to be best suited to the flow required within the cavity. If inserts are to be molded into place, they are positioned carefully on their locating studs or into the proper recesses in the mold cavity. The time for charging the mold may be lengthy, especially if there are a large number of inserts to be handled, or split cavities to be adjusted. For high-production work, economies sometimes can be realized by duplication of molds, whereby one set is

undergoing cure while the other is being unloaded and charged by the operator.

2. CLOSING THE MOLD: After the molds have been charged the inlet valve to the hydraulic system should be opened slowly and the molds carefully closed. The mold halves should not come together too rapidly for high-pressure gradients built up under these conditions would break insert holding pins and coring pins. Besides, a longer period will permit the escape of accumulated gases in the molds as well as bring the material up to correct molding temperature. Preheating molding materials before introduction into the mold will lessen mold closing time. A few preliminary trial runs will soon determine the best mold closing time, which varies from 10 seconds to more than a minute in some cases. There are restrictions imposed on mold closing time by the material, for some thermosetting compositions are so heat-reactive that their flowing qualities will be lost if this period is prolonged unnecessarily. In many molding establishments, low pressures (200 to 500 pounds per square inch) are applied first upon the ram for closing the molds, followed then by the application of the high pressure line (2000 to 3000 pounds per square inch) to develop full molding pressure. Lower pressures are required with high-frequency preheating. In transfer molding, the molds are fully closed before the material is introduced, flowing from the transfer pot through sprue, runners, gate, and then mold cavities.

3. BREATHING OR GASSING: A number of phenolic and urea type molding compositions require a short breathing or gassing period, after the molds have been closed, to permit the escape of such gases as air, steam, or ammonia. This step often reduces curing time and improves the quality and appearance of the finished article. Porosity and blisters are minimized and electrical properties improved. Sometimes 15 to 20 seconds elapse before breathing phenolic compositions, and often more than one gassing period is necessary. For certain "soft" phenolic compositions the molds are not closed fully but allowed to remain open for a distance of less than an inch, until the material is stiff enough to mold properly. So important is the feature of gassing the molds that recently developed equipments for fully-automatic compression molding make provisions for a breathing period in their cycle for thermosetting resins.

4. CURING: During the curing period, the desirable mechanical and electrical properties of the thermosetting composition are developed. Thermoplastic compositions do not require a curing period, though as soon as the material has flowed, the mold must be chilled. As the curing time may range anywhere from one-half to several minutes, this phase of the molding cycle is studied carefully to effect desirable properties within the shortest period of time. Thickness of piece, temperature, and the nature of the composition employed play an important part in determining the time of the curing cycle. Tabulated herewith are some of the disadvantages of undercure and overcure.